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REMOVAL OF BIOCHEMICALLY RESISTANT COMPOUNDS BY ADSORPTIONS-III

J. Carrell Morris, et al

Harvard University
Cambridge, Massachusetts

August 1964

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REMOVAL OF BIOCHEMICALLY-RESISTANT COMPOUNDS BY ADSORPTION-III

By
J. Carrell Morris
and
Walter J. Weber, Jr.

August, 1964

Final Technical Report

Division of Engineering & Applied Physics
Harvard University

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Robert A. Taft Sanitary Engineering Center
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INTRODUCTION

This is the third and final report on research in the Division of Engineering and Applied Physics at Harvard University undertaken to obtain information on the possible removal of organic pollutants from waste waters and incidentally from polluted natural waters by adsorptive processes. The research has been a part of the program of research sponsored by the Advanced Wastes Treatment Research Program, Division of Water Supply and Pollution Control, U. S. Public Health Service, in accordance with Contract SAph 76295 between Harvard University and the United States Public Health Service from May 15, 1961, to August 31, 1964.

During the first year of this research, studies were directed largely to an evaluation of the basic characteristics of adsorption of a number of typical individual persistent pollutants found in waste waters on a variety of selected solid adsorbents. Rates and equilibria of adsorption were studied for a great number of these simple systems and attempts were made to interpret the findings in the light of current theories of the adsorptive process.

It had been hoped in this initial study to find a solid adsorbent that would offer greater economy or utility than activated carbon. No such material was encountered, however, and so subsequent work was devoted more to studies of the range of utility and limitations in the use of activated carbon as an adsorbent.

The studies of the first year were conducted entirely in closed batch-type systems. The results of the batch experiments made it apparent that full utilization of the adsorptive capacity of activated carbon could best be obtained by continuous passage of waste-water through beds of the adsorbent, activated carbon, and that if such techniques were used, an adsorptive capacity better than 10% by weight should be obtained readily.

Accordingly, studies for the second year of the research were directed primarily to more detailed exploration of the behavior of activated carbon as an adsorbent for water pollutants.

Three main lines of investigation were followed. One was development of a wet-oxidation technique for reliable determination of small concentrations of organic carbon in water, for this was essential as a preliminary to investigation of the efficiency of activated carbon in adsorbing organic pollutants of unknown composition from waste waters. The second was an exploration of the effieiency of adsorption of single pollutants in activated carbon columns during continuous flow as a preliminary to the study of multi-component solutions. These studies were conducted using upward flow through the carbon columns at rates sufficient to expand the carbon beds into a fluidized condition and showed that the adsorption of organic materials in such fluidized columns was quite similar to that obtained in beds operated as conventional filters. Third, batch studies were extended to solutions containing two distinct types of solute and the occurrence of competition for adsorption in such solutions was shown.

During the current year the types of studies begun in the previous years have been extended further. Column studies have been undertaken with multi-component solutions to observe how solutions more nearly resembling waste waters behave in continuous flow operation. Additional batch studies with a wider variety of organic pollutants have been undertaken so that adsorptive characteristics of such materials might be related to their adsorptive properties in continuous-flow systems. Some work has been undertaken in an attempt to find out what types of organic pollutants are not adsorbed from waste waters by activated carbon.

Because of the large scope of the research and the vast number of organic materials that might be involved, none of the research topics that have been pursued, except possibly the determination of organic carbon, have been concluded with definitive thoroughness. A great deal has been learned about the characteristics of adsorption from dilute aqueous solution, a field of research that has never had the thorough and systematic treatment of gas-phase adsorption, but the information is not complete enough for conclusive generalizations. There are many gaps in the data and the implications of some studies have not been followed up sufficiently. Numerous instances are pointed out in the body of the report.

Nonetheless, it appears that in general the fundamental groundwork has been laid for more detailed and extended studies of adsorption by activated carbon on a larger scale. Advantageous possibilities for the use of activated carbon in adsorption; more practical studies are now needed to define efficient and economical conditions and procedures of operation.

This does not mean that fundamental studies in this area should be abandoned. New basic information and theory are always needed for stimulation and understanding. However, such studies should now be undertaken in smaller areas of interest with greater thoroughness and refinement.

CHAPTER ONE

ADSORPTION IN FLUIDIZED COLUMNS OF ACTIVATED CARBON - II

Description of the initial phases of an investigation of rates and capacities for adsorption in fluidized columns of adsorbent has been given in the second annual report.[1] Previously, factors of flow rate, particle size of adsorbent, and nature of adsorbent were investigated for solutions containing a single solute; a branched-chain sulfonated alkylbenzene served as the solute, while two types of activated carbon and an activated aluminum oxide were tested as adsorbents.

Additional experiments have been conducted during the past year to extend the previous studies to more complex, multiple-solute systems, to investigate competitive interactions between solutes and to provide needed information for evaluation of the fluidized carbon column as a technique for treating wastes containing varied types of organic substances. As a part of the last objectives the influences of changes in pH, temperature, and concentration of solute on the effectiveness of operation of fluidized carbon in columns have also been investigated.

EXPERIMENTAL

Apparatus

The apparatus used in these continued experiments was similar in all essential details to that used in the earlier stages of the investigation. A Lucite tube 1-inch in diameter was fitted at the bottom with a velocity-head-dissipation chamber filled with 2-mm glass beads. A 140-mesh, stainless-steel screen separated the adsorbent in the column from the glass beads in the dissipation chamber. For most studies, the experimental columns were packed with 45 grams of carbon placed in a tube which was 3 feet in length.

The settled depth of this amount of carbon was about 22 cm or 9 inches. Longer columns were required for some experiments in which a greater quantity of carbon was used to allow ample head space for expansion of the carbon.

Flow to the column was regulated by means of two valves, one a needle valve for fine control, in the 0.5-inch feed-line from a constant-head tank. A float valve in the constant-head tank controlled the flow of solution from 200-liter plastic storage reservoirs connected in parallel. Effluent flow from the top of the column passed through an air-gap to prevent siphoning and pressure fluctuations in the column, through a 1-liter settling tank for removal of any fine material carried over with the effluent, and into one of several volume-calibrated, 200-liter collecting reservoirs.

Adsorbents and Adsorbates

Columbia LC coconut carbon and an activated carbon obtained from the Pittsburgh Chemical Company - the same carbons as those employed previously in column studies - were used for the current investigations. The Columbia carbon was used in the majority of the experiments.

Prior to use each adsorbent was separated by thorough sieving into uniform particle sizes; then portions of suitable size-range were washed in distilled water to remove leachable impurities and adherent powder and were next dried at 105°C. The size chosen for most extensive study comprised particles passing a United States Standard Sieve No. 50 and retained on a No. 60 sieve; the mean particle diameter for this size range is 0.273 mm.

A number of adsorbates typical of different classes of organic pollutants were studied. Ultrawet K, a branched-chain sulfonated alkylbenzene obtained as a 93-%-active-material sodium salt from the Atlantic Refining Company, was the most commonly used solute. The average molecular weight of the Ultrawet K based on its ultraviolet absorbance, using a molar absorptivity of 12.9×10^6 cm^2/mol at 225 mμ for sulfonated alkylbenzenes[2], was found to be 396 grams. The Ultrawet K thus has a somewhat higher molecular weight than the other sulfonated alkylbenzenes used in the earlier stages of the investigation. A "dodecylbenzenesulfonate", obtained from the Continental Oil Company, and Ultrawet D.S. had been used in the previous experiments; these materials were found to have an average molecular weight of 372 grams.[1]

Other solutes studied included nonylphenoxypolyethoxyethanol (a nonionic surfactant), 2-sec-butyl-4,6-dinitrophenol (a herbicide-insecticide), phenyl-N,N-dimethylphosphorodiamidate (an insecticide), and 2,4-dichlorophenoxyacetic acid (a herbicide). These substances were obtained from the Dow Chemical Company.

Sodium dodecylsulfate, a Matheson, Coleman and Bell product, was better than 95% pure in dodecylsulfate and 99.5% in total alkylsulfate by analysis.

Triethanolamine, quinine sulfate, phenol, 2,4-dichlorophenol, and sodium p-toluenesulfonate were obtained as reagent grade products from Eastman Organic Chemicals.

Analytical Methods

Ultraviolet absorption[2] was used for determination of the concentration of the sulfonated alkylbenzene, Ultrawet K, in experiments in which this solute was the only adsorbate present in solution. When this substance was

a component of solutions in which other solutes caused interference with the ultraviolet method the Longwell and Maniece modification of the Jones method using methylene blue was employed.[3] Ultraviolet absorption as previously described[2] was used also for determination of p-toluenesulfonate.

Many of the other substances could also be determined readily by light absorption in the visible or ultra-violet region. Quinine exhibits a maximum in light absorption at 330 mμ with a molar absorptivity of 4.70×10^6 cm^2/mol; 2,4-dichlorophenol has a maximum in absorption at 284 mμ with a molar absorptivity of 2.05×10^6 cm^2/mol; and 2-sec-butyl-4, 6-dinitrophenol (DNOSBP) has a maximum at 375 mμ with a molar absorptivity of 13.80×10^6 cm^2/mol. The absorption of each of these substances was found to follow the Beer-Lambert law for the range of concentrations studied. Thus measurements of absorbance at the indicated wave-lengths permitted rapid and accurate determination of the corresponding substances.

The remaining solutes were used solely as components of complex mixtures of organic compounds, and determinations of their individual concentrations were not made. Effectiveness of adsorption in experiments with complex mixtures was evaluated in terms of the over-all removal of organic pollutants which was measured in terms of organic carbon. Determinations of organic carbon were made according to the wet oxidation technique previously described.[4]

Experimental Method

An accurately weighed quantity of carbon, usually about 45 grams, was mixed well with approximately one liter of distilled water and the mixture was introduced into the plastic column which was set in place in the experimental apparatus. Distilled water was run through the apparatus and the

column to permit adjustment of the flow to the desired rate with a needle valve. The valve immediately following the needle valve in the flow train was then closed, the carbon was allowed to settle, and the water in the column was drawn down through a sample port to a level approximately 1/4 inch above that of the settled carbon. The distilled water was then drained from the remainder of the system.

The feed solution to be used was then made up in the storage reservoirs and introduced to the constant head tank.

The run was then started to allow upflow of the feed solution through the carbon bed at the rate previously set with the needle valve. Samples of the effluent were taken at appropriate intervals after displacement of the initial volume of distilled water remaining in the column at the beginning of the run. In addition to "instantaneous" sampling, samples of the integrated effluent were taken from the storage reservoir used to collect the solution from the top of the column.

Temperature control internal to the system was deemed unnecessary in the studies in which the effect of temperature was not being specifically investigated because the room temperature, and consequently the temperature of the feed solution, varied but little from approximately 28°C to 30°C. On the basis of temperature effects noted previously[5], it was concluded that this slight variation would have no significant effect on the results of the column studies.

RESULTS

Solute Effects

a) Type of solute. - Previous experiments on adsorption by carbon in fluidized columns had been conducted with highly-branched sulfonated alkylbenzenes. It was of interest to explore possible differences in adsorption

pattern for different solutes upon passage through fluidized carbon columns and to ascertain whether observed differences can be correlated with characteristics found through more readily accomplished measurements on batch systems. Hence, in one experiment parallel columns were run with two solutes having considerably different molecular weights but of the same chemical class of compound. The solutes used were Ultrawet K and sodium p-toluenesulfonate. The latter is the simplest alkylbenzenesulfonate with a molecular weight of 171 for the anion; the former is a branched-chain alkylbenzenesulfonate with about 15 carbon atoms in the alkyl group.

One reason for the choice of these two solutes was that rates of adsorption and capacities for adsorption on activated carbon from solute solution have been studied previously for p-toluenesulfonate and for materials very similar to the Ultrawet K in batch-type systems and marked differences in these adsorption characteristics have been observed.[5,6]

Figure 1-1 presents data for the adsorption of Ultrawet K from a solution with an initial concentration of 73.3 μmoles per liter in a column containing 45 grams of 0.273-mm Columbia carbon; this quantity of the 0.273-mm carbon had an unexpanded column-height of approximately 22 cm. The flow rate for the study was 2.5 gpm/ft^2. The form of the curve representing the relative effluent concentration, C/C_om as a function of time is quite similar to that obtained previously for other highly-branched sulfonated alkylbenzenes under similar experimental conditions.[1]

In Figure 1-2, a comparison of the curve shown in Figure 1-1 for Ultrawet K is made with a similar curve for sodium p-toluenesulfonate. The initial concentration of p-toluenesulfonate in the solution used for this experiment was 79.6 μmol per liter; carbon size and quantity as well as flow-rate were identical to the experiment with Ultrawet K.

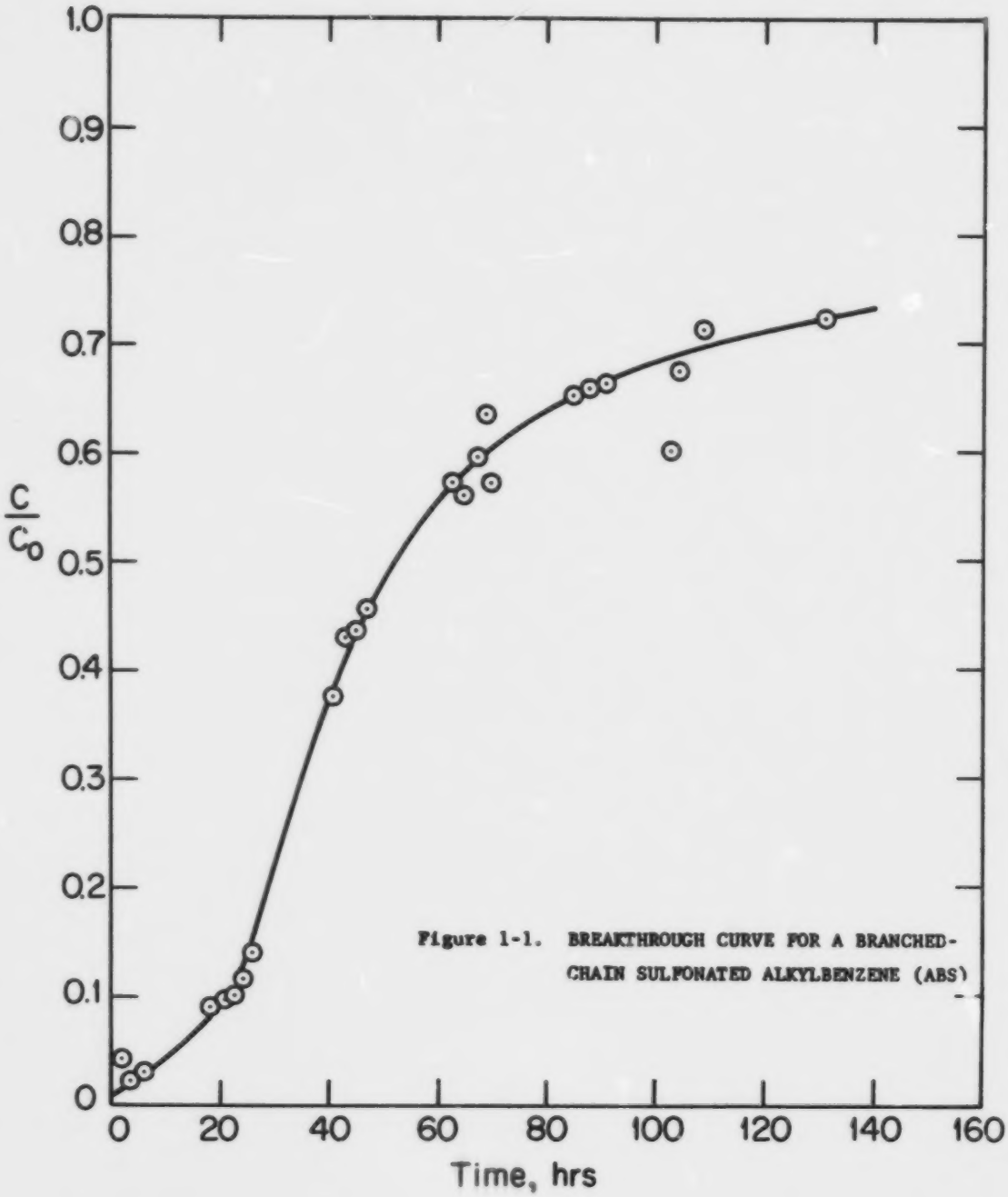

Figure 1-1. BREAKTHROUGH CURVE FOR A BRANCHED-CHAIN SULFONATED ALKYLBENZENE (ABS)

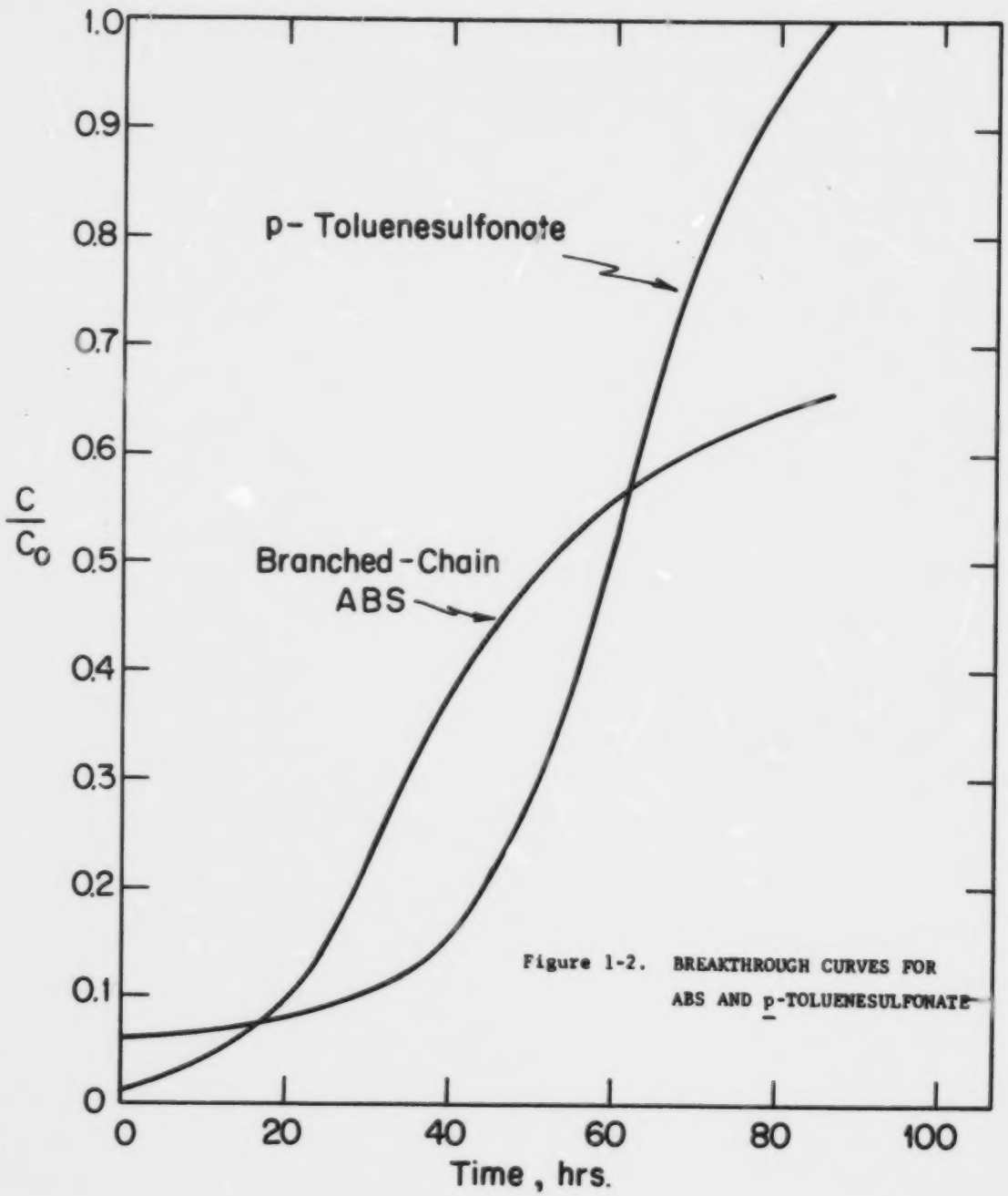

Figure 1-2. BREAKTHROUGH CURVES FOR ABS AND p-TOLUENESULFONATE

Several points of comparison should be noted. First, there was an initial leakage of p-toluenesulfonate considerably greater than that for the ABS, the leakage of the p-toluenesulfonate being 6% of its influent concentration to about 2% for the ABS. Second, the effluent leakage for the p-toluenesulfonate increased very little for the first twenty hours of operation whereas that for the ABS increased almost from the start and after sixteen hours of operation became greater than the leakage from the p-toluenesulfonate column. Third, as a corollary to the second point, the total break-through of p-toluenesulfonate was much sharper than that of the ABS. After about sixty hours the uptake from the ABS solution was once again more effective than from the p-toluenesulfonate solution. Fourth, after about one hundred hours the total integrated uptake from the two solutions had been about the same, but about one-third of the influent ABS was still being removed whereas the capacity for adsorption of p-toluenesulfonate had apparently been exhausted.

The fact that the Ultrawet K is taken up more completely during the very early stages of the run than is the p-toluenesulfonate is in accord with the findings of previous equilibrium studies in batch systems. During the first few hours of the experiments the concentration of each solute in the water passing up through the expanded bed of fresh carbon is reduced to a low figure beyond the first few inches of the column. Previous investigations of the equilibria of adsorption on carbon have indicated that the energy of adsorption for a high molecular weight sulfonated alkylbenzene is greater than for p-toluenesulfonate.[6] That is, effective adsorption is observed for much smaller concentrations with the ABS than with p-toluenesulfonate. Thus, removal by adsorption of the last traces of the high-molecular-weight Ultrawet K should be considerably easier than complete clean-up of the p-toluenesulfonate.

The increasing leakage of the ABS in contrast to that of the p-toluenesulfonate over the first twenty hours of column operation can be associated with the relative rates of adsorption observed in batch studies on these solutes. Because of the slow rate of penetration of the ABS into the interior surfaces of the carbon granules the active external points soon reach a significant fraction of saturation and subsequent adsorption is less rapidly effective. With the p-toluenesulfonate a relatively rapid migration of adsorbed material to the interior permits renewal of active external surface and substantial maintenance of efficienty of adsorption for a longer period. When nearly full capacity has been attained, there is a relatively sharp break-through.

Maintenance of adsorption capacity in the column adsorbing ABS beyond the time required to exhaust the column adsorbing p-toluenesulfonate is expected on the basis of the greater adsorption capacity for the former material found in the batch equilibrium studies.

The separate column studies with Ultrawet K and p-toluenesulfonate thus give indication that at least qualitative prediction of column behavior may be possible from knowledge of batch-system behavior, at least for cases in which a single-solute solution is passed through the column.

b) Concentration of Solute.- Figure 1-3 presents break-through curves for three experiments in which the effects of different concentrations of Ultrawet K were studied. The flow-rate for each experiment was 2.5 gpm/ft^2, and each column contained 45 grams of 0.273-mm Columbia carbon.

The effect of concentration on break-through of solute is as would be expected, that is, the higher the concentration the more rapid the break-through. Yet it may be noted that at the points corresponding to $C/C_o = 0.1$ the total weights of ABS adsorbed were about the same in all three runs.

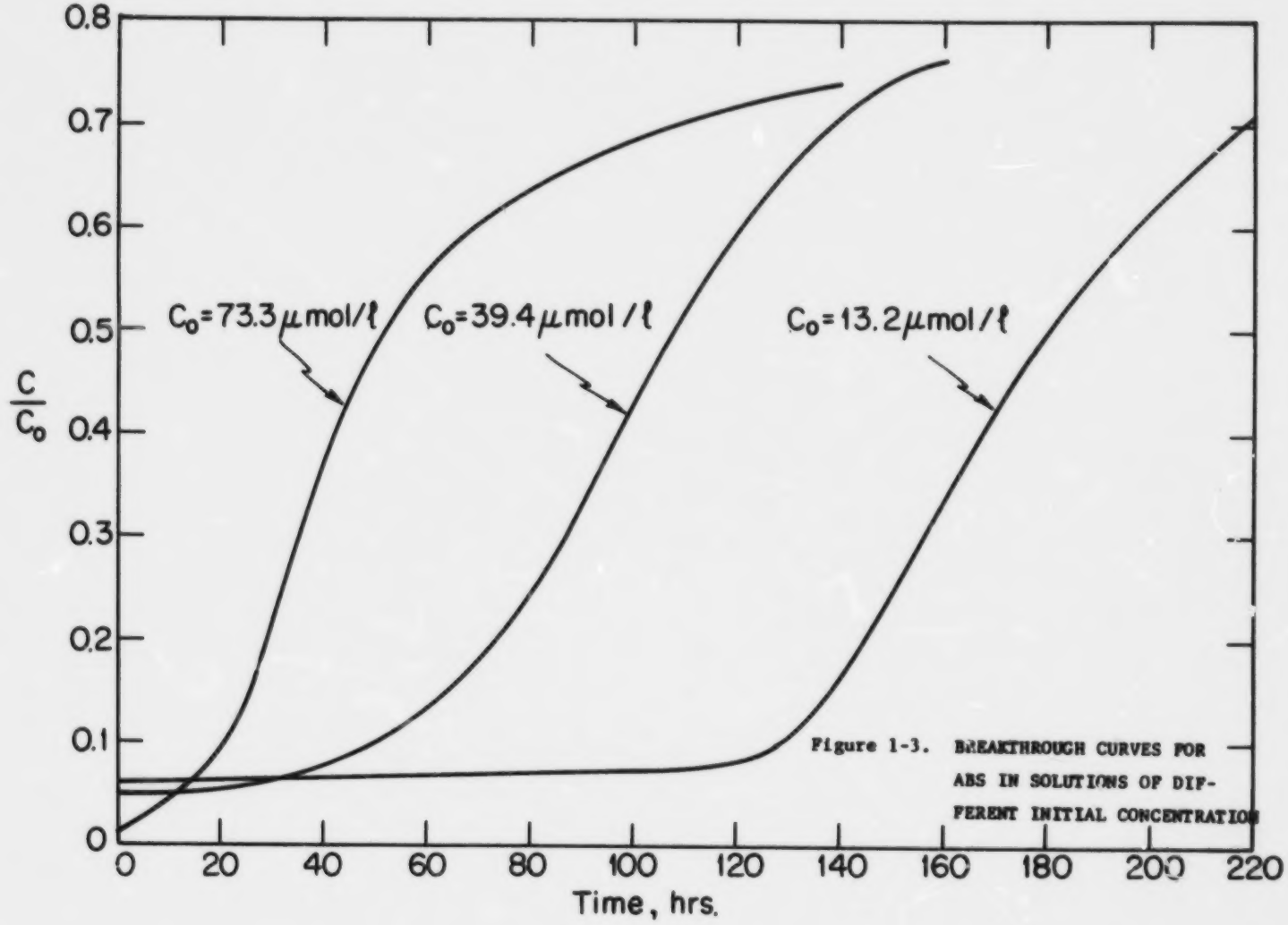

Figure 1-3. BREAKTHROUGH CURVES FOR ABS IN SOLUTIONS OF DIFFERENT INITIAL CONCENTRATIONS

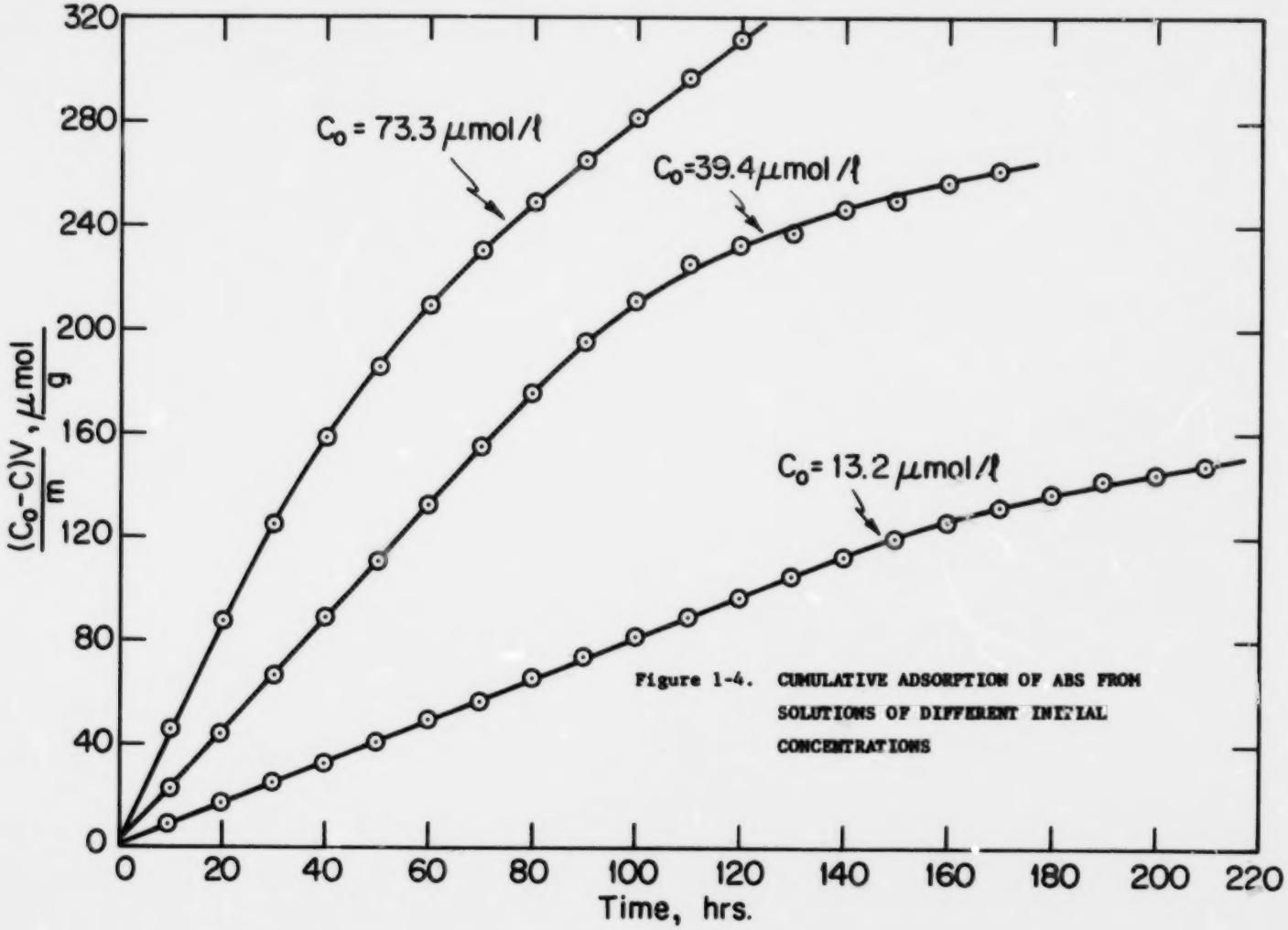

Figure 1-4. CUMULATIVE ADSORPTION OF ABS FROM SOLUTIONS OF DIFFERENT INITIAL CONCENTRATIONS

Although leakage appears greater at the smaller influent concentrations, it should be noted that the actual effluent concentrations at zero time were 0.85, 1.5 and 0.8 ppm for increasing influent concentrations. It thus appears that initial effluent concentrations will be determined primarily by the depth of the adsorption column rather than the influent concentration.

One other noteworthy point is that with the lowest influent concentration, 13.2 μmol/l or 5.2 mg/l, better than 90% adsorption was maintained with just a nine-inch settled depth of carbon for more than 5 days. This would mean about 40 days effective operation for a five-foot settled depth with this concentration of material to be removed.

Figure 1-4 shows total quantity of solute removed from solution by the 45 grams of carbon in each experiment. As would be expected on the basis of the increased driving force for transfer with increased concentration of solute in solution, [1] and the greater capacity of the carbon at the greater influent concentration, both the rate of uptake and total quantity of solute removed is greater at the higher influent concentrations of Ultrawet K for the same period of time. After 100 hours of operation, the carbon in the experiment in which the influent concentration of solute was 73.3 μmol per liter had removed a total quantity of solute equal to approximately 11% of the weight of the adsorbent, and for the experiment with C_o = 13.2 μmol per liter the solute removed was about only 3% of the weight of the carbon. Since it was impractical to carry on the experiments at the lower initial concentrations until the carbon was exhausted full capacities as a function of concentration could not be measured.

Temperature Effects

Three experiments were carried out with Ultrawet K as solute at solution temperatures of 36°C, 28°C, and 16°C. Flow-rates of 2.5 gpm/ft^2 were maintained

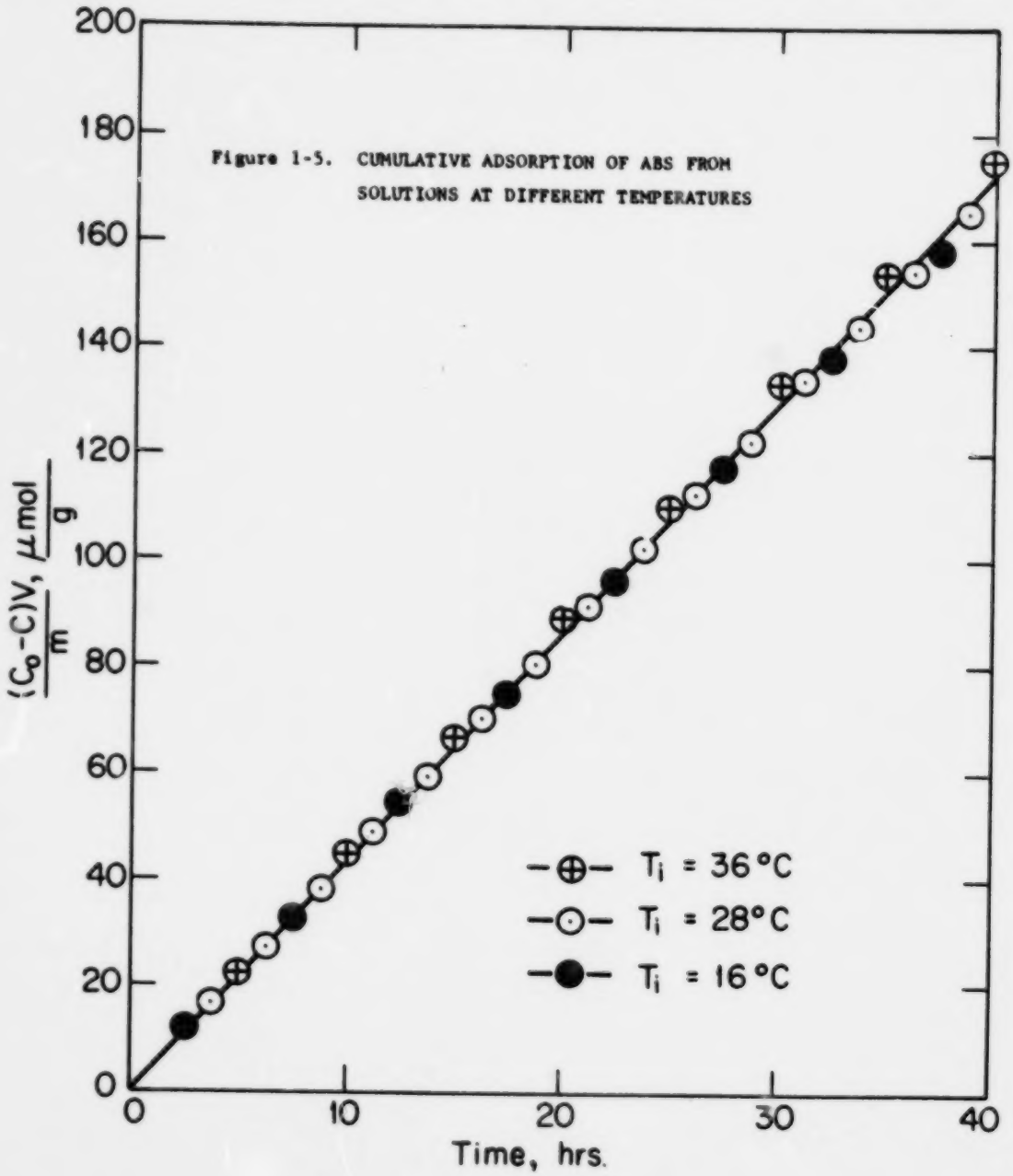

Figure 1-5. CUMULATIVE ADSORPTION OF ABS FROM SOLUTIONS AT DIFFERENT TEMPERATURES

in columns containing 45 grams of 0.273-mm Columbia carbon. The initial concentrations of solute were closely the same, in the range of 77-80 μmols per liter. The experiment at 28°C was at room temperature; for the experiment at 16°C the influent was chilled by means of a conventional Freon compressor with the cooling coil immersed in the constant-head tank; a blade-type heater was used in the constant-head tank to heat the influent for the experiment at 36°C. Each temperature given is an average of the temperatures of the influent and effluent for a column. Temperature differences between the influent and effluent for each experiment were less than 3°C.

Little difference in the total uptake of solute as a function of time was observed for any of the temperatures studied, as shown in Figure 1-5. Such a result is to be expected, for the total uptake is primarily a function of the adsorptive capacity of the carbon with beds of sufficient depth and depends very little on the rate of adsorption. Adsorptive capacity does not change greatly over a small temperature range such as that used in these experiments.

The effect of temperature should be noted most significantly for column work in the steepness of the breakthrough portion of the curve of relative effluent concentration as a function of time. At lower temperatures, where the rate of adsorption is less, increasing leakage should begin sooner and a more gradual approach to full saturation should be observed. If one looks closely at the experimental points in Figure 1-5 there is some indication of this effect, for the data at 36°C beyond twenty-five hours lie consistently above the mean curve and more nearly maintain the linear relationship characteristic of complete absorption, while the data at 18°C lie consistently below the mean curve indicating increasing leakage through the column.

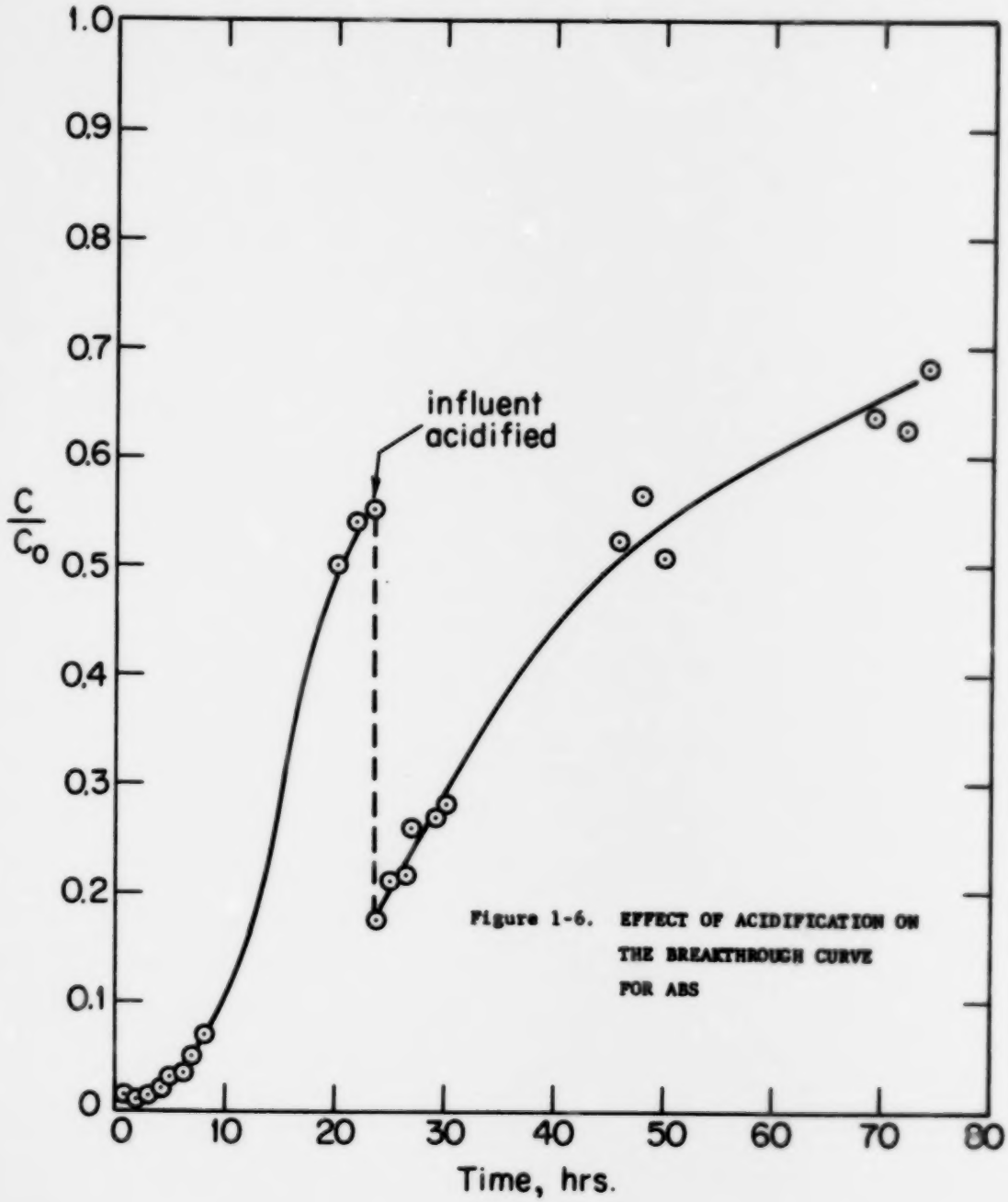

Figure 1-6. EFFECT OF ACIDIFICATION ON THE BREAKTHROUGH CURVE FOR ABS

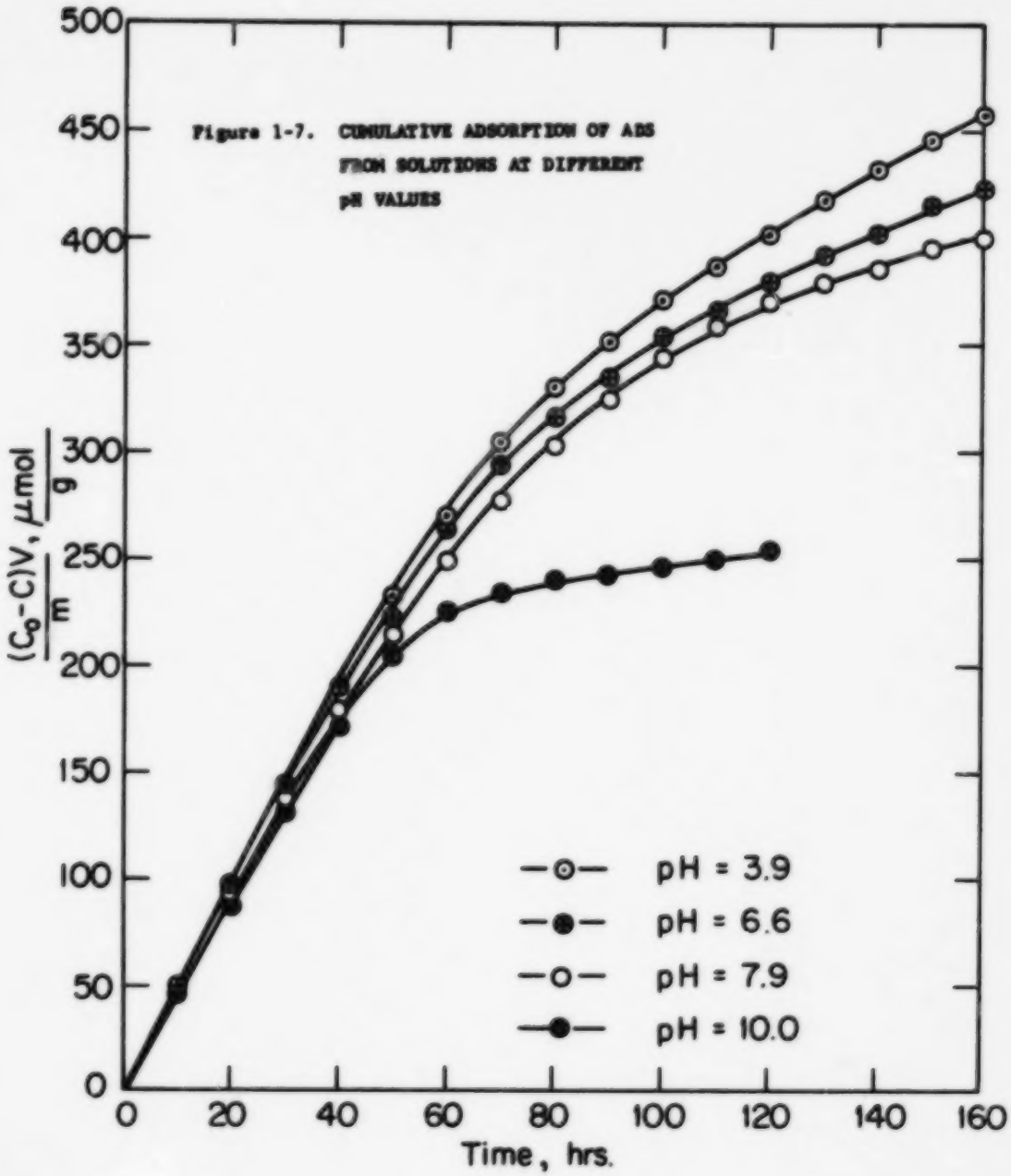

Figure 1-7. CUMULATIVE ADSORPTION OF ABS FROM SOLUTIONS AT DIFFERENT pH VALUES

pH Effects

A preliminary investigation of the effect of solution pH on uptake of solute by carbon in a fluidized bed was made by passing a solution of Ultrawet K, with an unadjusted pH slightly below neutral, at a flow rate of 2.5 gpm/ft^2 through a column containing 45 grams of 0.359-mm Columbia carbon. The larger particle size was used so that more rapid break-through would be obtained. When the value of C/C_o for the experiment reached 0.55, the pH of the influent was decreased to 2.5 by addition of concentrated phosphoric acid. As illustrated by the data for this run plotted in Figure 1-6, the decrease in leakage after this acidification of the influent was dramatic.

To test the effect of solution pH more extensively, four experiments were conducted at different pH values, each with a column containing 45 grams of 0.273-mm Columbia carbon and a flow-rate of 2.5 gpm/ft^2. The initial concentration of solute, Ultrawet K, in each experiment was within the range from 79 to 81 μmol per liter. Adjustment of pH in the solutions to values of 3.9, 6.6, 7.9, and 10.0, respectively, was accomplished by appropriate addition of phosphoric acid or phosphate. The pH values given are for the influents to the columns.

Data for the pH studies are presented in Figure 1-7, which shows the total quantities of solute removed from solution by the carbon as a function of time. There is a notable difference between the total amounts of solute removed from solution in the experiments at the highest and lowest pH values tested, the total amount at any time being considerably greater at low pH. The experiments at intermediate pH levels are observed to fit into the pattern of increasing removal with decreasing pH. The observed dependence of solute removal on pH for the column studies accords with previous work

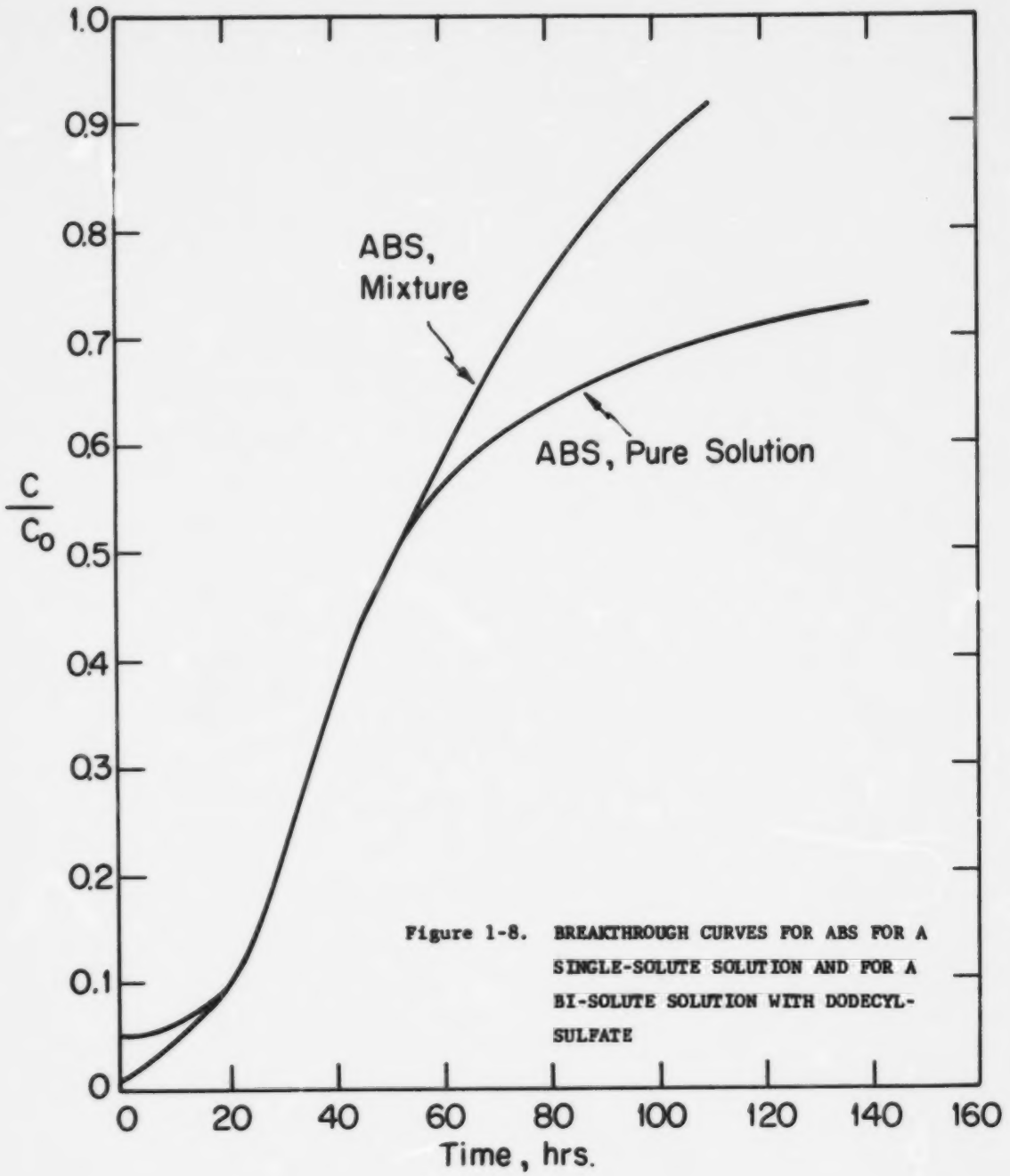

Figure 1-8. BREAKTHROUGH CURVES FOR ABS FOR A SINGLE-SOLUTE SOLUTION AND FOR A BI-SOLUTE SOLUTION WITH DODECYL-SULFATE

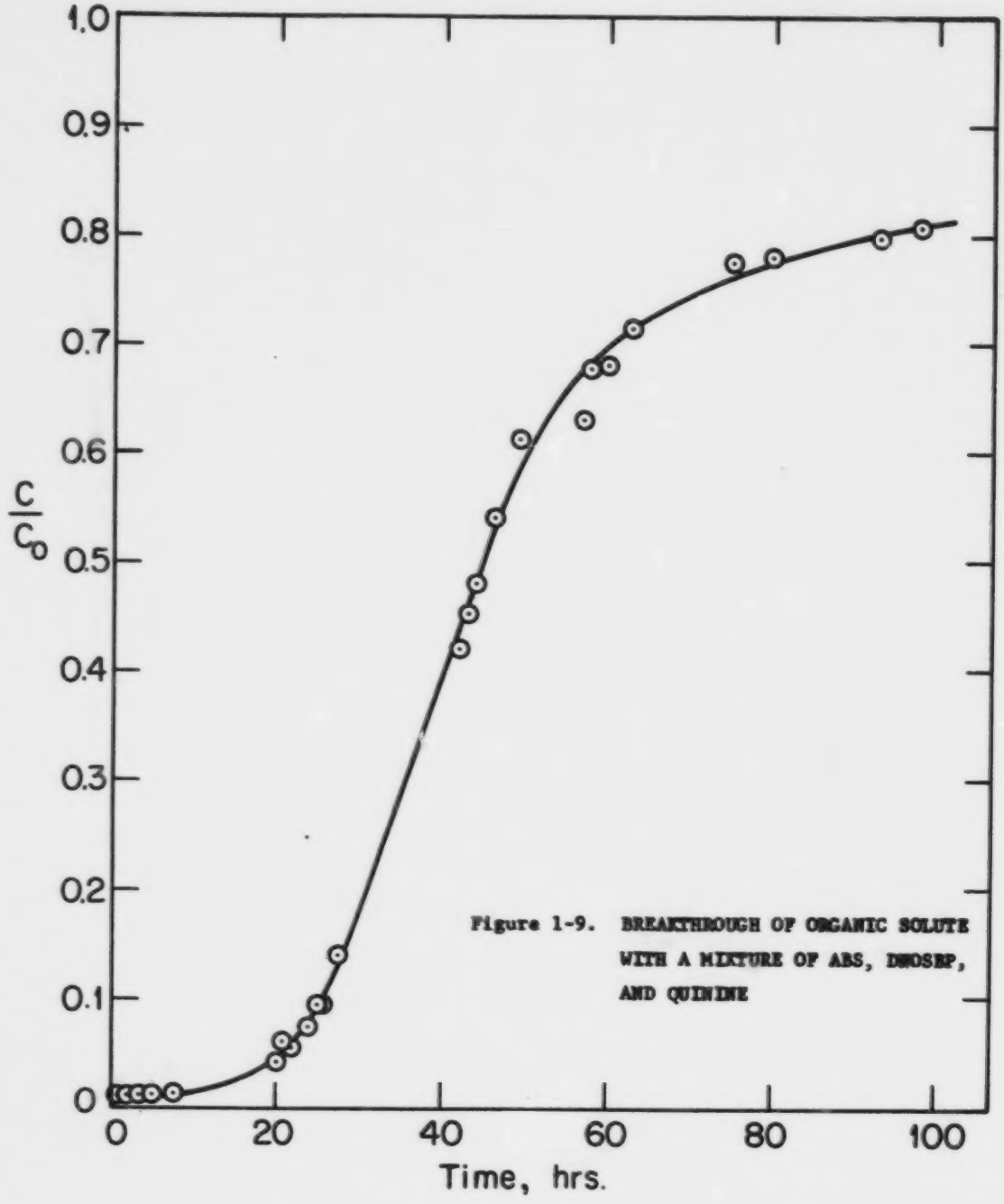

Figure 1-9. BREAKTHROUGH OF ORGANIC SOLUTE WITH A MIXTURE OF ABS, DNOSBP, AND QUININE

in which both rates and final positions of equilibrium for adsorption of sulfonated alkylbenzenes on the experimental carbon in batch-type systems were found to increase with decreasing pH.[5,6]

Even so, in order to show marked changes in adsorption with pH it was necessary to go to very high or low pH values. Over the pH range of particular interest, 6 to 8, differences in adsorption efficiency were minor. More pronounced effects may be obtained with other types of pollutants, but in general it can be expected that normal pH variations will not affect significantly the operation of activated carbon columns.

Multi-Component Solutions

That solutes in multiple-component solutions compete with one another for adsorption on carbon has been demonstrated for agitated non-flow systems.[7] Studies have been carried out during the present investigation to explore the nature and extent of competitive interactions in continuous flow systems. Such studies are significant for evaluation of the suitability of continuous-flow adsorption systems for waste-water treatment, for rarely does the waste-water to be treated contain but one organic pollutant. Rather, waste waters are likely to be heterogeneous mixtures of complex organic substances of different chemical types or classes.

In these investigations, solute mixtures of two, three, four, and eight components have been studied.

a) Two Components. - Some pronounced effects of sodium dodecylsulfate on the adsorption of a sulfonated alkylbenzene in batch systems have been noted previously.[7] Hence, mixtures of sodium dodecylsulfate and the branched sulfonated alkylbenzene, Ultrawet K, were employed as solute in initial studies of adsorptive competition on columns.

A solution containing 71.6 μmol per liter of Ultrawet K and 75.0 μmol per liter of dodecyl sulfate was passed at 2.5 gpm/ft^2 through a column containing 45 grams of 0.273-mm Columbia carbon. Because a simple analytical technique for dodecylsulfate in dilute solution was not available only the concentration of the ABS was determined in the effluent. Figure 1-8 presents the break-through curve found for the Ultrawet K (ABS) in this study and compares it with a break-through curve for a pure solution of the ABS. The experiment with the ABS alone was carried out under identical conditions with a solution containing 73.3 μmol per liter of ABS.

It is apparent from the curves shown in Figure 1-8 that the presence of the dodecylsulfate has a marked effect on the over-all adsorption of the sulfonated alkylbenzene. However, the competitive effect appears to be not significant in the early stages of the run; a major difference between the break-through curves for ABS in mixed and pure solution is noted only after about fifty-five hours of operation of the column. During the first fifty-five hours the carbon apparently had sufficient capacity for both solutes so that little effective competition for adsorption occurred. Since in this experiment the dodecylsulfate was added to the ABS concentration rather than replacing part of it, whatever dodecylsulfate was adsorbed would be expected to reduce the adsorptive capacity for ABS.

b) Three Components. - To test further the effects of solute interactions on adsorption in fluidized columns from solutions containing mixtures of organic compounds, a column study was run with a solution containing three different classes of organic compounds. The influent solution consisted of Ultrawet K at a concentration of 43.6 μmol per liter, 2-sec-butyl-4,6-dinitrophenol (DNOSBP) at a concentration of 31.8 μmol per liter, and quinine

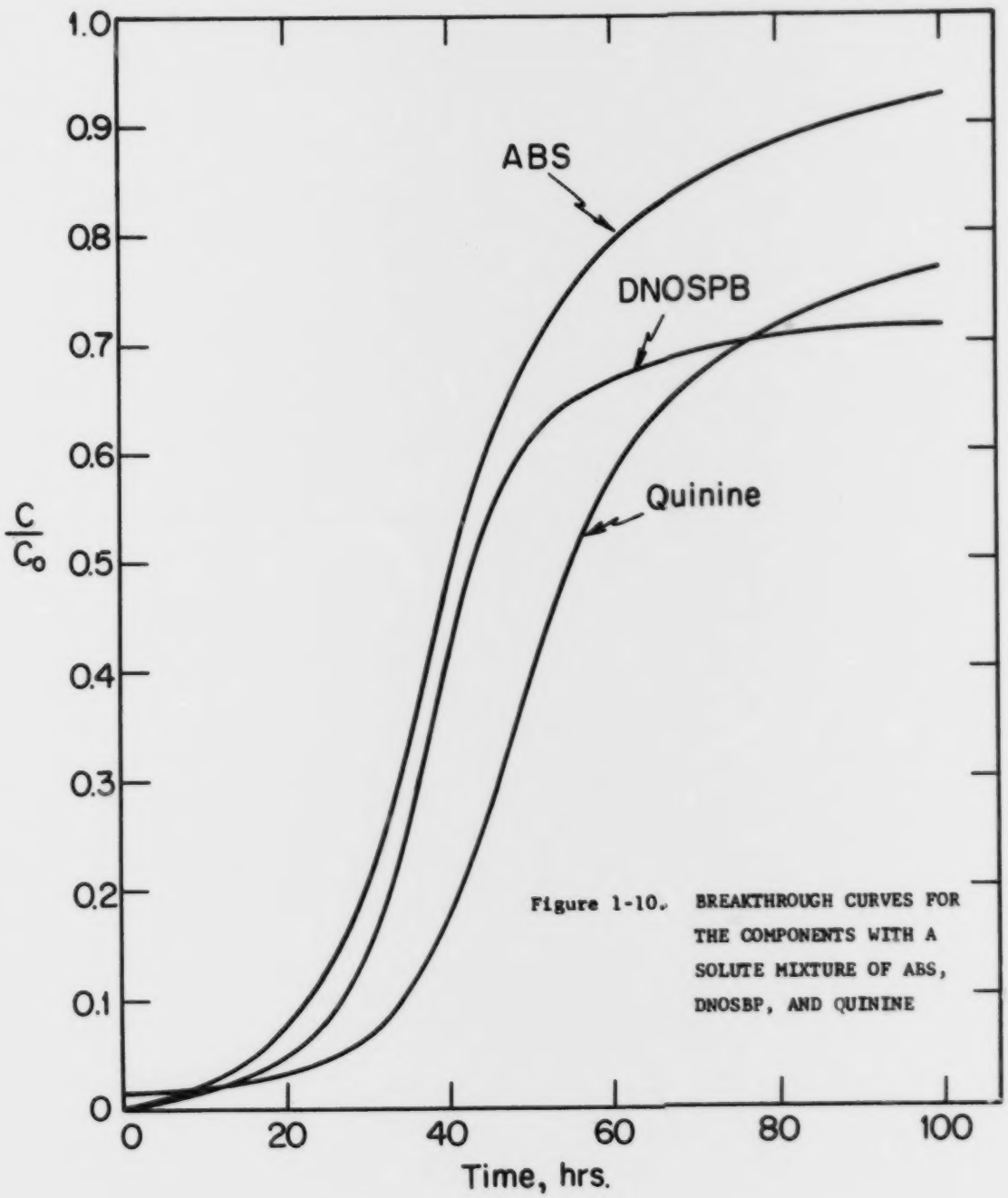

Figure 1-10. BREAKTHROUGH CURVES FOR THE COMPONENTS WITH A SOLUTE MIXTURE OF ABS, DNOSBP, AND QUININE

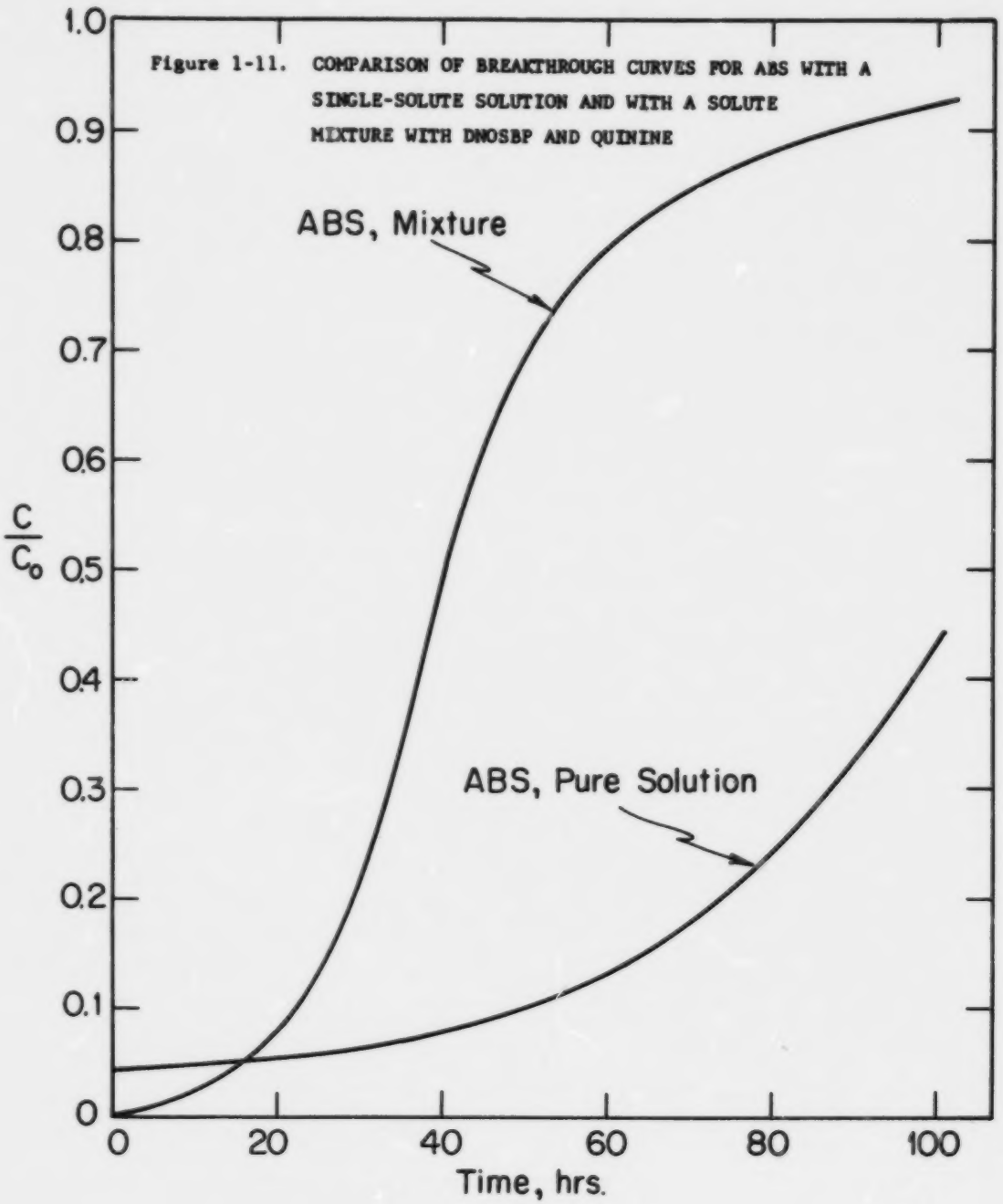

Figure 1-11. COMPARISON OF BREAKTHROUGH CURVES FOR ABS WITH A SINGLE-SOLUTE SOLUTION AND WITH A SOLUTE MIXTURE WITH DNOSBP AND QUININE

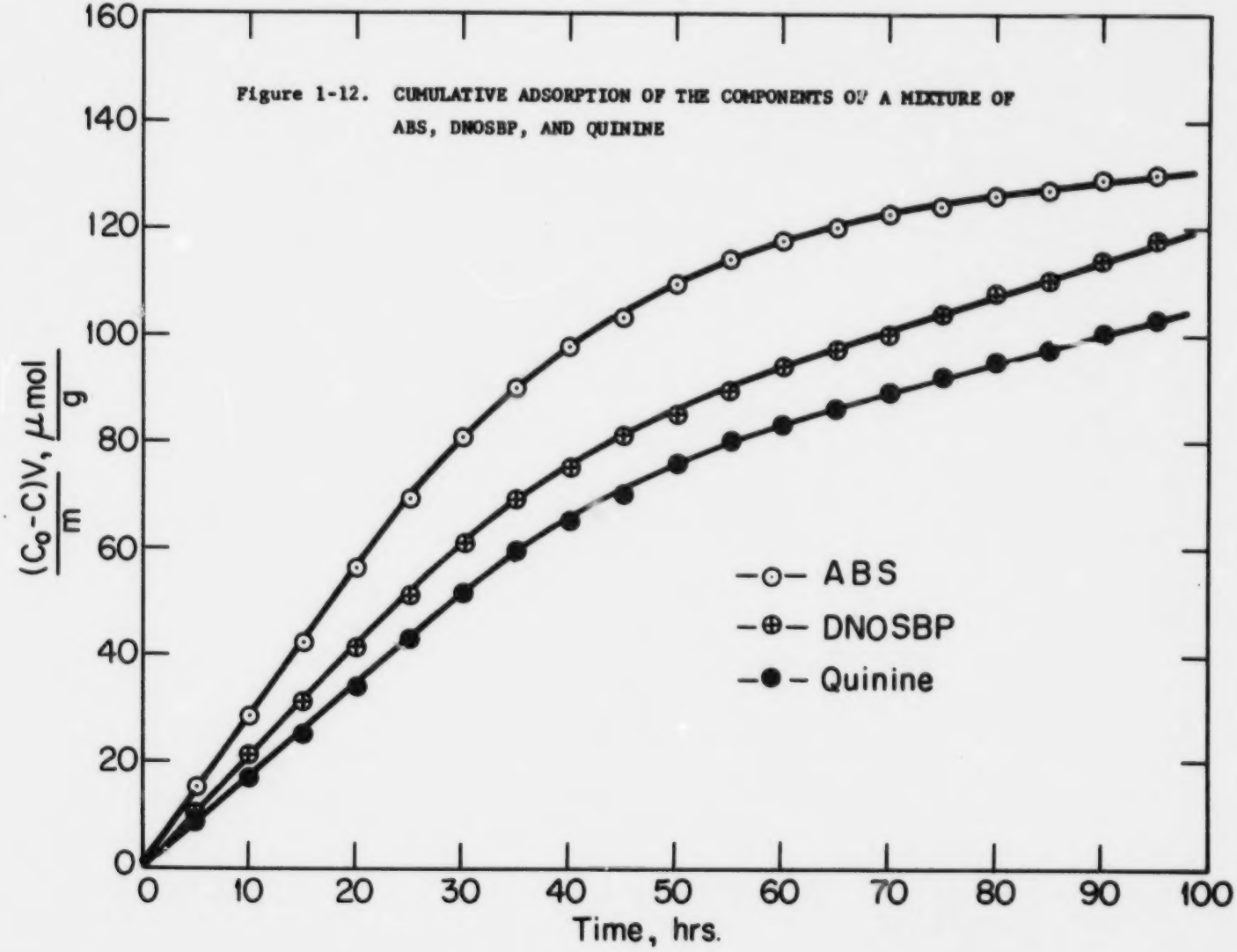

Figure 1-12. CUMULATIVE ADSORPTION OF THE COMPONENTS OF A MIXTURE OF ABS, DNOSBP, AND QUININE

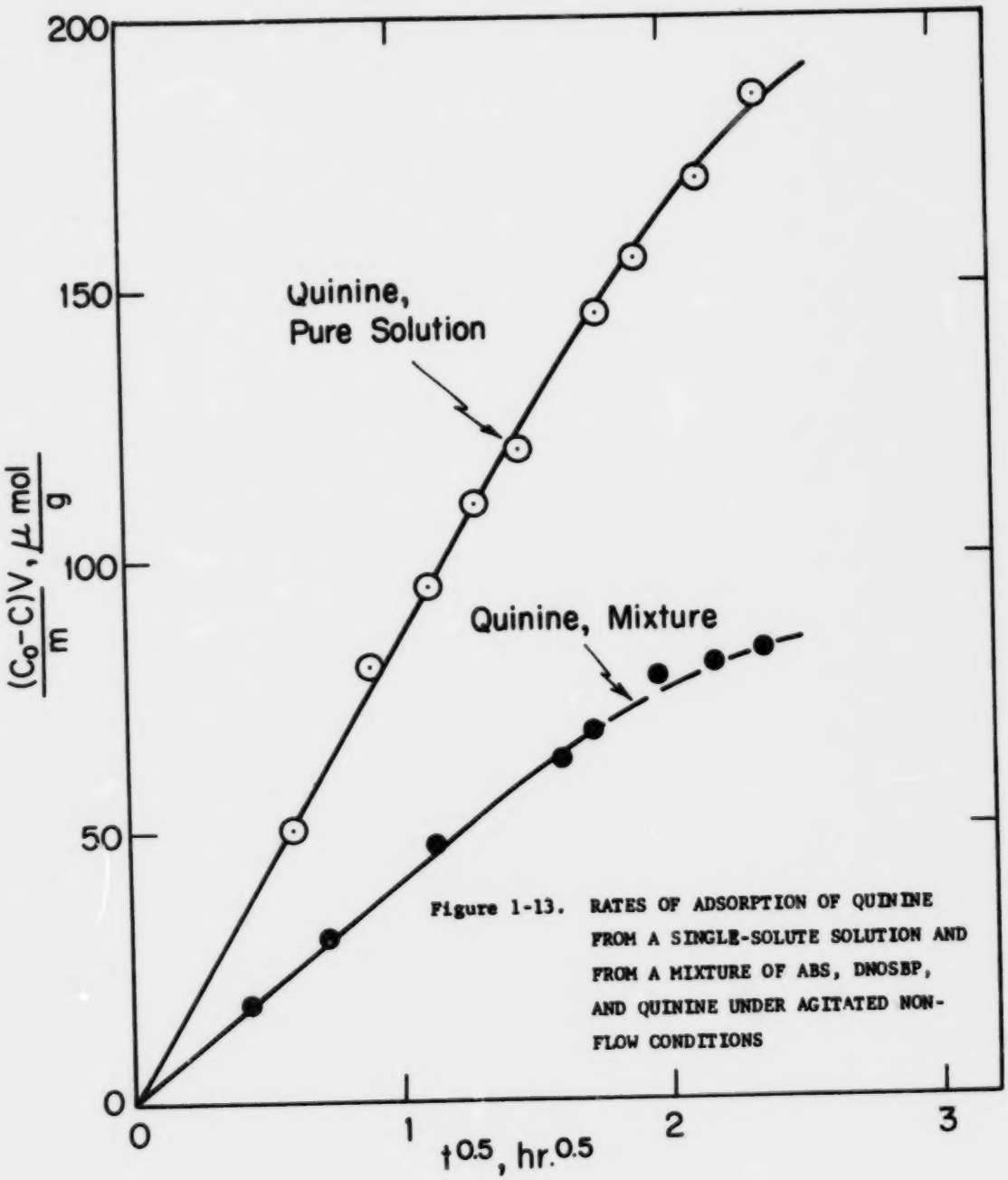

Figure 1-13. RATES OF ADSORPTION OF QUININE FROM A SINGLE-SOLUTE SOLUTION AND FROM A MIXTURE OF ABS, DNOSBP, AND QUININE UNDER AGITATED NON-FLOW CONDITIONS

sulfate at a concentration of 26.9 μmol per liter (as the quinine base). The flow-rate for this experiment was 2.5 gpm/ft^2 and the column consisted of 45 grams of 0.273-mm Columbia carbon.

Analyses for concentration of the ABS in the mixed solution were carried out with the methylene blue procedure mentioned previously; no interference from the quinine or the DNOSBP was experienced with this procedure. Determinations of quinine and DNOSBP were made by spectrophotometric measurements at 330 mμ and 375 mμ, respectively. The molar absorptivities for these substances at their respective wave lengths for peak adsorption have been listed earlier in this report. At 375 mμ the molar absorptivity of the quinine was 0.07 x 10^6 cm^2/mol, and that for the DNOSBP at 330 mμ was 4.71 x 10^6 cm^2/mol. Determinations of individual concentrations of these two solutes thus required measurement of each sample at each of the two wavelengths, and simultaneous solution of two absorbance-concentration equations.

The over-all break-through curve for the mixture is shown in Figure 1-9. The concentration ratio plotted in Figure 1-9 is for the total concentrations of all of the organic solutes present in the solution, computed by summing the results of the individual determinations. The over-all break-through curve is quite similar in pattern to those observed previously for single-solute solutions.

Figure 1-10 shows break-through curves for each of the components of the mixture. The break-through for the ABS in the mixture is much more rapid than is that for a pure solution of similar initial concentration of ABS. This fact is illustrated by the curves plotted in Figure 1-11. The break-through curve shown in Figure 1-11 for the single-solute solution was

obtained under identical flow and adsorbent conditions with a 39.4 μmol per liter solution of the Ultrawet K.

On the other hand the break-through is not as rapid as would have been expected for ABS alone at a concentration equal to 102 μmol per liter, the sum of the component concentrations. In fact the curve is rather similar to that obtained with 73 μmol per liter of ABS. This tends to indicate some enhancement of total absorptive capacity for the mixed components, like that found earlier in the batch studies of competitive adsorption.

There were no single-solute column studies for quinine and DNOSBP with which the other curves in Figure 1-10 might be compared.

The curves shown in Figure 1-10 do not bring out completely the adsorption picture for this experiment with a multi-component solution. Figure 1-10 alone gives the impression that the amount of ABS adsorbed was less than the amount of DNOSBP adsorbed, and that the amount of quinine adsorbed was greatest of all. Actually, because of the initial differences in concentration the amounts of individual solutes removed from the mixed solution flowing through the column were the reverse of this order. This is shown by the cumulative uptake plots in Figure 1-12.

Comparison of Figure 1-12 with Figure 1-4 shows that the extent of adsorption of the ABS from the mixture was less than that from a pure solution of approximately the same concentration for long periods of operation. For example, the quantity of ABS adsorbed from the mixture after one hundred hours was about 130 μmols per gram of carbon, while for a pure solution of similar initial concentration of ABS the quantity adsorbed after one hundred hours was about 210 μmols per gram of carbon (Figure 1-4). However the total organic matter adsorbed after one hundred hours - the sum of ABS, DNOSBP and quinine was 350 μmol/gram.

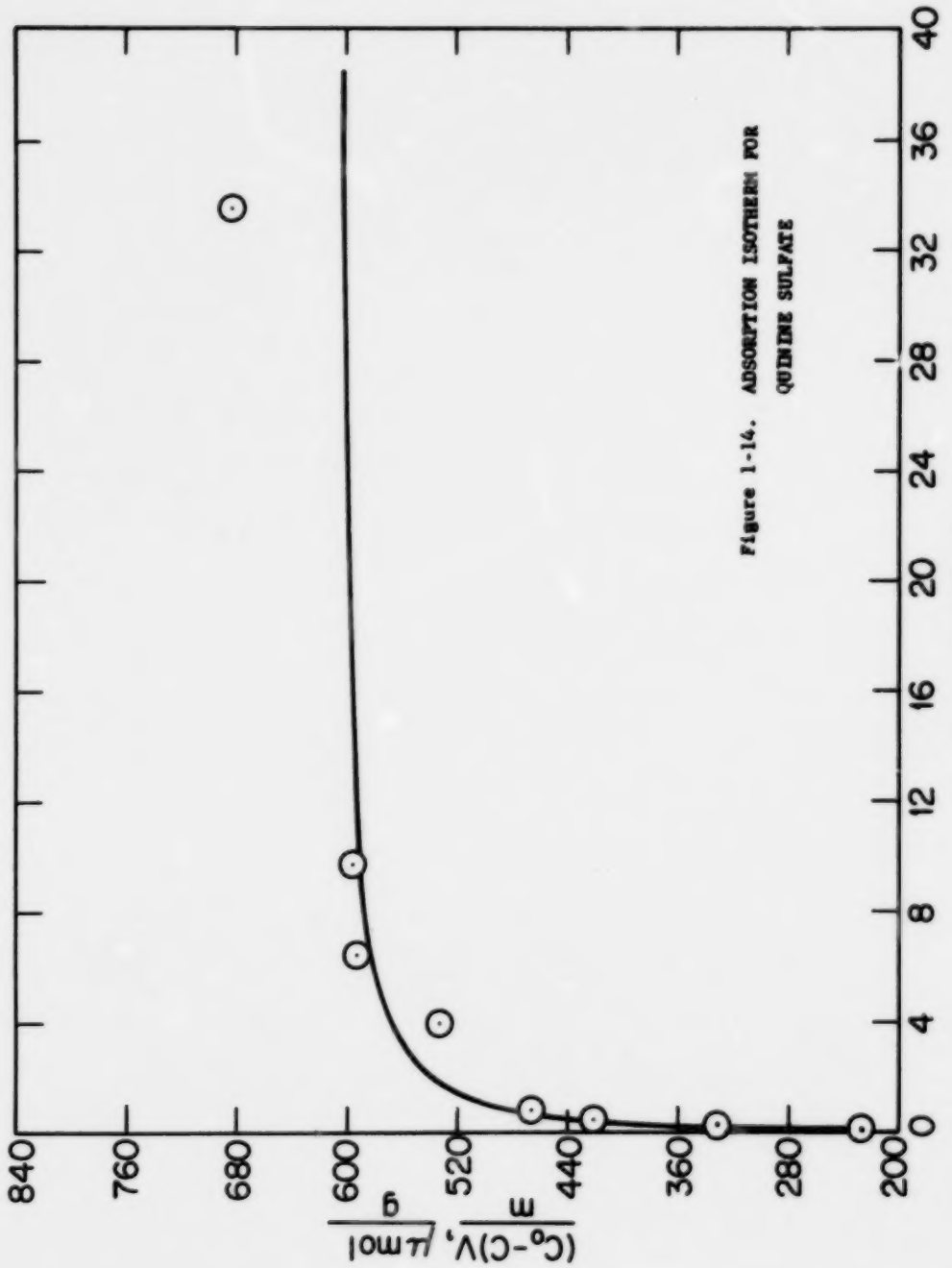

Figure 1-14. ADSORPTION ISOTHERM FOR QUININE SULFATE

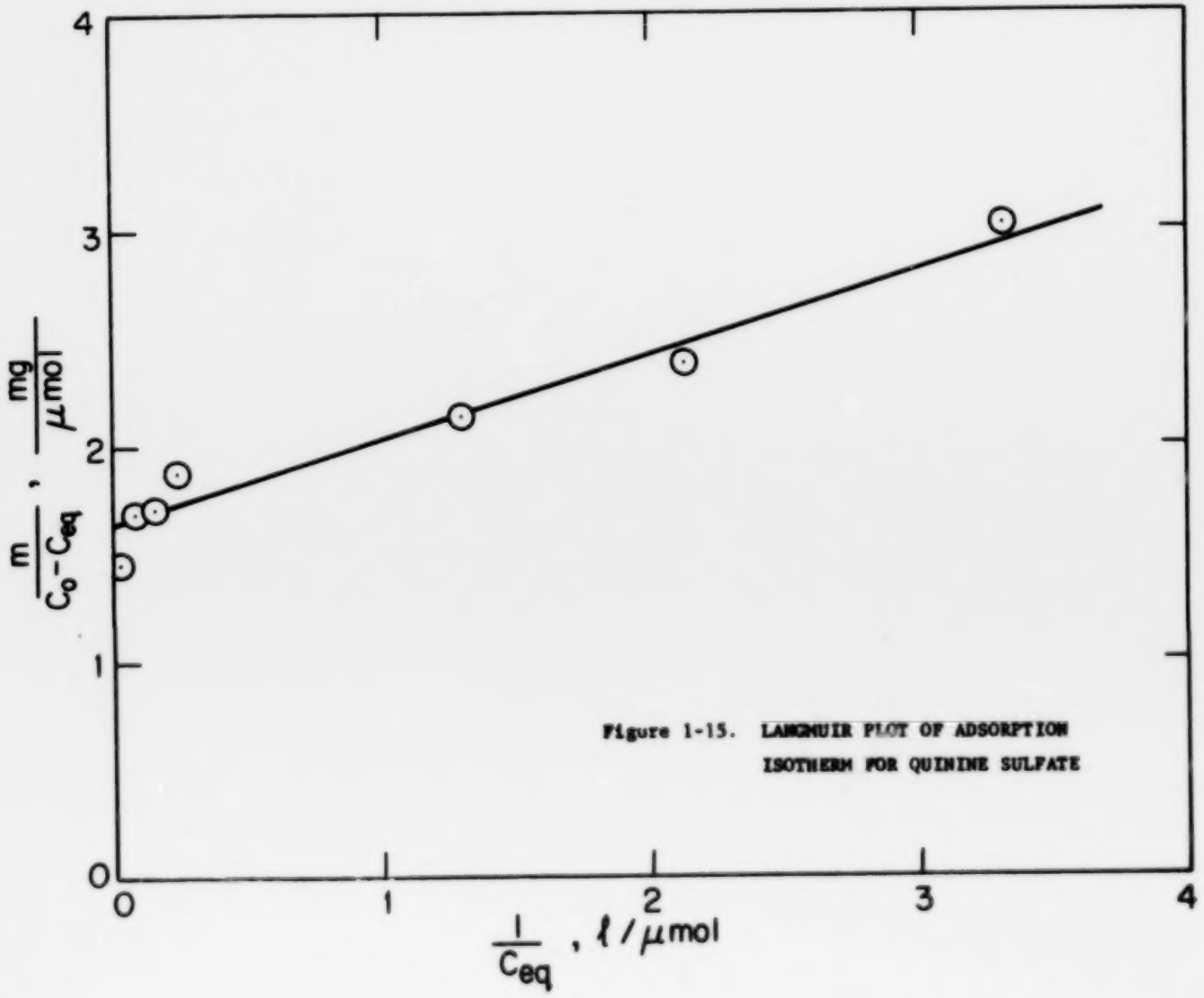

Figure 1-15. LANGMUIR PLOT OF ADSORPTION ISOTHERM FOR QUININE SULFATE

In an effort to determine whether the observed adsorption patterns for the mixture could be predicted from batch-system studies, kinetic and equilibrium experiments with non-flow systems were conducted using the same mixture of the three solutes and also with solutions of the three individual components in each of which the initial concentration of solute was the same as its initial concentration in the mixture.

Figure 1-13 shows a plot of data for the rate of adsorption of quinine, obtained from the batch-type experiments. Both the pure solution and the mixture studies were conducted at 29°C. Fifty mg of 0.273-mm Columbia carbon per liter was used in the experiment with the pure quinine solution and 250 mg per liter of the same carbon was used for the experiment with the multi-component solution to take account of the difference in total concentration of organic solutes present. The data in Figure 1-13 have been linearized for the initial portions of the rate studies by plotting the amount removed from solution as a function of the square root of the time, according to an intraparticle-transport rate step.[5]

There is a clear reduction in the rate of uptake of the quinine from the mixture as compared to the rate for the pure solution. Yet it should be noted also that while the amount adsorbed per unit of carbon from the multi-component solution in an hour was about half that in the pure solution, the mole fraction of quinine in the multicomponent solution was only about 0.23.

Similar data were obtained for the other solutes; rate constants derived from the data are listed in Table 1-1. The values for the relative rate constant, k. are squares of slopes of plots of the type shown in Figure 1-13. These data indicate that the rate of adsorption of DNOSBP is by far the most

adversely affected in the mixture. There seems to be some tendency for all the rates to reduce to a more nearly common value in the multi-component solution. This is also indicated by the parallel slopes of the break-through curves in Figure 1-10.

Table 1-1

Relative Rates of Adsorption from Pure Solutions and Multi-component Solution

0.273-mm Columbia carbon, agitated non-flow system, 28°C

	Relative rate constant, k, $[(\mu mol/g)^2/hr] \times 10^{-3}$	
Solute	Pure solution	Mult'-component solution*
sulfonated alkylbenzene	3.60	1.85
quinine	7.23	1.60
2-sec-butyl-4,6-dinitrophenol	57.60	0.26

*mixture: 43.6 μmol/l sulfonated alkylbenzene, 26.9 μmol/l quinine, 31.8 μmol/l 2-sec-butyl-4,6-dinitrophenol

Isothermal equilibrium studies at 30°C for the individual component solutions were also conducted using 0.273-mm Columbia carbon. A plot of the equilibrium adsorption data for quinine is given in Figure 1-14. The curve fitted to the points in Figure 1-14 is a calculated Langmuir-type curve; the linearized form is given in Figure 1-15.

Langmuir constants for all three solutes are listed in Table 1-2; X is the amount of adsorbed material per gram of carbon, X_m is the limiting value of X for monolayer adsorption according to the Langmuir model, C is the concentration of solute in solution at equilibrium, and b is a constant expressive of the energy of adsorption and equal to the reciprocal of the concentration at which adsorption is equal to $X_m/2$.

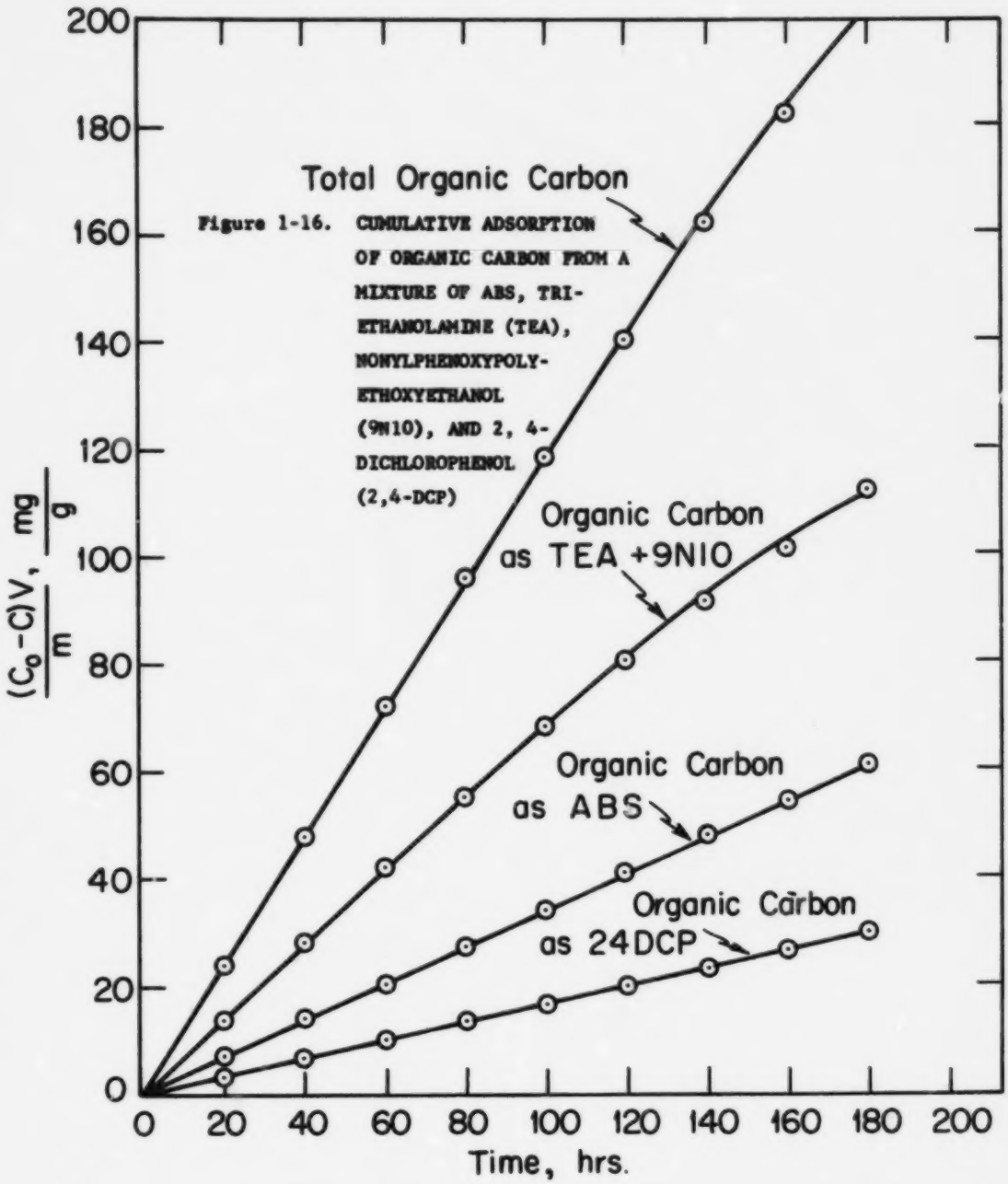

Figure 1-16. CUMULATIVE ADSORPTION OF ORGANIC CARBON FROM A MIXTURE OF ABS, TRIETHANOLAMINE (TEA), NONYLPHENOXYPOLYETHOXYETHANOL (9N10), AND 2, 4-DICHLOROPHENOL (2,4-DCP)

Table 1-2

Langmuir Constants for Adsorption Isotherms

0.273-mm Columbia carbon, 30°C

Langmuir equation: $X = \frac{X_m bC}{1+bC}$

Solute	X_m, $(\frac{C_o - C_{eq}}{m})$, $\frac{\mu mol}{g}$	b, $\frac{1}{\mu mol}$
sulfonated alkylbenzene	455	0.478
quinine	605	4.13
2-sec-butyl-4,6-dinitrophenol	1,850	0.174

Attempted correlation of these batch studies with the previous column studies is difficult and probably premature, for neither the batch nor the column studies have been sufficiently complete. The only direct comparison to be made between the batch studies on the rates of adsorption and the continuous-flow studies is with the slopes of the breakthrough curves for the columns. Unfortunately the slopes of the breakthrough curves with the shallow beds used in these studies have not been well enough defined to make such a comparison meaningful. Conversely, the relative amounts of uptake for the individual solutes in the mixture might be compared with data on individual adsorption isotherms in the multi-component solution, but these latter data have not yet been obtained.

It is tempting to relate the great reduction of rate of uptake of DNOSBP in the multi-component solution as compared with pure solution with the comparatively low "b" value obtained in the isotherm studies and with

the reduced capacity for adsorption shown in the mixed-column studies. Yet, it must be admitted that fitting of the Langmuir equation to the equilibrium adsorption data for a substance like DNOSBP that exhibits an apparent X_m value equal to better than 40% of the weight of carbon is theoretically meaningless, since the monolayer assumption is certainly invalid.

For the present, then, these results must simply be added to the fundamental data on adsorptive behavior being accumulated for later use when more complete delineation of the systems has been accomplished.

c) Four Solute Components.- Another column study was conducted with a solution containing four different classes of organic compounds, both to determine the adsorptive patterns of some other types of solutes in multi-component solutions and to investigate break-through effects in deeper columns of a carbon more suitable for practical use in waste-water treatment.

A multiple-component solution containing 24.5 mg/l Ultrawet K, 15.5 mg/l triethanolamine, 16.9 mg/l 2,4-dichlorophenol and 53.7 mg/l nonylphenoxy-polyethoxyethanol was passed upward through a one-inch column containing 200 grams of 0.273-mm Pittsburgh carbon, at a rate of 2.5 gpm/ft^2. The expanded height of the carbon column was 209 cm. In addition to routine determinations for concentrations of total organic carbon, ABS, and 2,4-dichlorophenol in the effluent from the column, several 20-liter samples of the effluent were concentrated by vacuum distillation and analyzed by infra-red spectrophotometry.

Figure 1-16 is a plot of data for the uptake of organic material by the Pittsburgh carbon during this 180-hour experiment. The data have been plotted as in terms of the organic carbon removed from solution as a function of time. It was possible, as illustrated in Figure 1-16, to account for the fractions of organic carbon existing as ABS and 2,4-dichlorophenol because

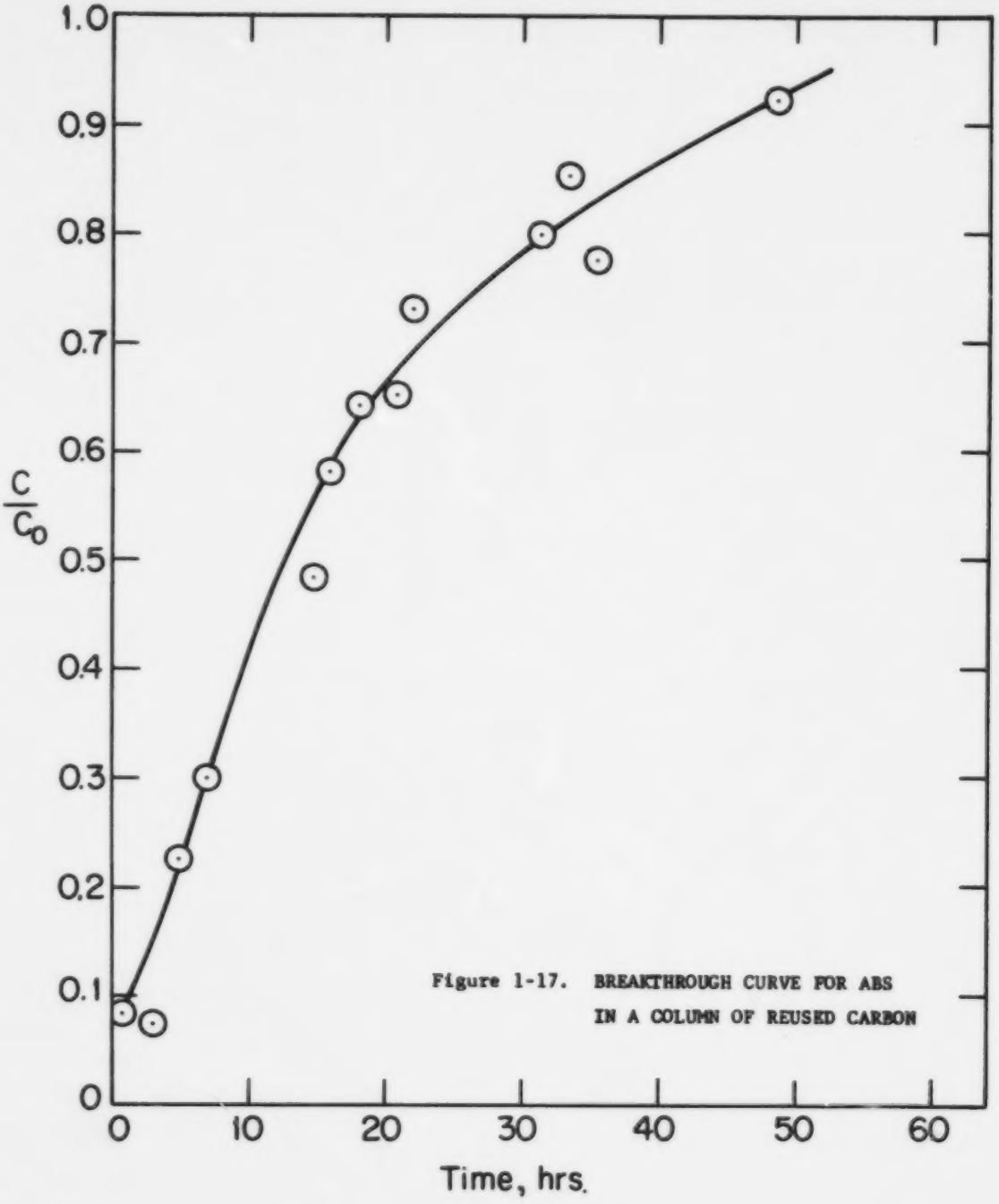

Figure 1-17. BREAKTHROUGH CURVE FOR ABS IN A COLUMN OF REUSED CARBON

these materials were determined individually. Although one fraction is represented as being composed of triethanolamine plus nonylphenoxypoly-ethoxyethanol (9N10), it should be kept in mind that infrared analyses showed complete uptake of 9N10 and considerable leakage of triethanolamine.

After about 150 hours of operation it became difficult to maintain the flow-rate of 2.5 gpm/ft^2 with the available head of 10 ft because of increased density of the carbon and clogging of the material in the column. At 180 hrs. it became impossible to hold the rate with the experimental apparatus and the run was terminated.

After 180 hours the C/C_o value for total organic carbon in the effluent had reached a value of only about 0.2. No significant concentrations of ABS or 2,4-dichlorophenol were found in the effluent up to this point by standard determinations. The periodic infrared analyses of concentrated effluent indicated that the only material being carried over in the effluent in any significant amount was the triethanolamine; approximately 50% of this material was passing completely through the column.

If the weight of the organic carbon in the mixture of organic solutes is taken as one-half the total weight of organic material, then as shown by Figure 1-16 the total amount of organic material removed from solution by the Pittsburgh carbon during the 180-hour run was about 400 mg per gram or a tremendous capacity of 40%-by-weight for the carbon to this point. To check this, a mass balance was run by removing the carbon from the column and drying it in a very thin layer at 105°C for 24 hours. The carbon was weighed after drying and found to weigh 279.5 grams! Thus the mass balance confirmed the very high capacity of 40%-by-weight. The good capacity realized in this experiment indicates that very high capacities with resulting economy in cost of carbon may be realized for some pollutants.

On the other hand, the early breakthrough of triethanolamine shows that some selectivity in removal of pollutants will be observed in practice and give some indication of the types of compounds that may not be effectively removed by carbon. Batch studies of rate of adsorption and adsorption equilibria should be carried out with triethanolamine.

D) Eight Solute Components

One column study was run with a very complex mixture of assorted classes of organic solutes. The solutes comprising the mixture, along with their respective concentrations in the influent, are listed in Table 1-3.

Table 1-3

Composition of Eight-Component Solute Mixture

Solute	Concentration in influent, mg/ℓ
phenol	2.4
quinine	9.3
dodecylsulfate	7.2
sulfonated alkylbenzene	10.6
2-sec-butyl 1-4,6-dinitrophenol	6.0
2,4-dichlorophenoxyacetic acid	5.5
nonylphenoxypolyethoxyethanol	16.5
phenyl N,N'-dimethylphosphorodiamidate	5.0

The column used in this experiment contained 100 grams of 0.273-mm Pittsburgh carbon, and the flow rate was 2.5 gpm/ft^2. Total organic carbon was the only analytical measure used to determine the effectiveness of the column.

Continuous flow was maintained for approximately one hundred hours; then experimental difficulties forced termination of the experiment - for some unexplainable reason prolific microbiological growths developed in the

influent solution, presumably made up largely of resistant substrates. At the termination of the run the value of C/C_o for total organic carbon had reached a level of about 0.1, and the total quantity of organic carbon removed from solution up to the time of termination was 8.5 grams. Thus the capacity attained by the adsorbent, up to the point when the experiment was stopped, was on the order of 16% on the assumption that the weight of organic matter was twice the organic carbon.

Self Regeneration of Activated Carbon

In a previous study it had been noted that activated carbon tended to regain some of its "initial capacity" upon standing, out of solution. It was assumed that this phenomenon occurred as a result of continued transport of solute within the pores of the carbon.(6) In further exploration of this phenomenon, carbon from one of the previous column experiments with Ultrawet K (the carbon used in the high-concentration run during the concentration-effect studies) was dried at 105°C for 48 hours and stored for two weeks. After drying the quantity of carbon weighed 52.1 grams, whereas its initial weight before use in the concentration-effect study had been 45 grams. The carbon was then replaced in a column and a solution containing 77.1 μmol/l of Ultrawet K was passed through it at a rate of 2.2 gpm/ft^2.

The results of this experiment are shown in Figure 1-17. While the carbon apparently did regain some of its "initial capacity" in that a typical break-through curve starting near $C/C_o = 0$ was found, the gain in capacity was not great, as indicated by the rapid and complete break-through after a relatively short period.

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CHAPTER TWO

ADSORPTION OF ORGANIC PESTICIDES ON CARBON

Environmental dispersal of organic pesticides has been a matter of much recent and widespread concern. The increased use of organic pesticides in agricultural, domestic, and industrial applications and the consequent increase in the occurrence of these materials in water and wastes have brought about a potential hazard for the health and well-being of the public.(1)

Adsorption by carbon appears to have promise as a technique for removing potentially harmful pesticides from waters and wastes. Accordingly, previous studies of rates and equilibria of adsorption have been extended to a number of representative pesticides or substances molecularly related to them.

Pesticide materials chosen for study include compounds of different chemical classes, typical of various types of herbicides, acaricides, and insecticides. The pesticides studied, along with some of their significant properties, are listed in Table 2-1.

Table 2-1

Selected Organic Pesticides

Compound	Primary Application	Molecular Weight	Approximate Solubility in Water at 25°C, mg/l
2,4-dichlorophenoxyacetic acid	herbicide	221.0	900
2,4,5-trichlorophenoxyacetic acid	herbicide	255.5	280
2-(2,4,5-trichlorophenoxy)-propionic acid	herbicide	269.5	180
2-sec-butyl-4,6-dinitrophenol	herbicide, insecticide	240.2	52
2-cyclohexyl-4,6-dinitro-phenol	acaricide, insecticide	266.2	10
1-naphthyl N-methylcarbamate	insecticide	201.2	99
O,O-diethyl-O-p-nitrophenyl phosphorothioate	acaricide, insecticide	291.3	24

As shown in Table 2-1, the chemical classes represented by the pesticides studied include thiophosphates (O,O-diethyl-O-p-nitrophenyl phosphorothioate), carbamates (1-naphthyl N-methylcarbamate), dinitrophenols (2-sec-butyl-4, 6-dinitrophenol and 2-cyclohexyl-4,6-dinitrophenol), and chlorophenoxy acids (2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid, and 2-(2,4,5-trichlorophenoxy) propionic acid).

The O,O-diethyl-O-p-nitrophenyl phosphorothioate (Parathion) was obtained from the American Cyanamid Company, the 1-naphthyl-N-methylcarbamate (Sevin) was obtained from the R. A. Taft Sanitary Engineering Center (U.S. Public Health Service), and the remainder of the compounds were obtained from the Dow Chemical Company. All compounds as obtained were described by the suppliers as being chemically "pure" relative to the active chemical agent.

Columbia LC coconut carbon was used as the adsorbent in all experiments with the pesticides. Prior to use in the experiments, the adsorbent was separated by thorough sieving into uniform particle sizes, after which portions of suitable size-range were washed in distilled water to remove any leachable impurities and adherent powder, and dried at 105°C. The size-range chosen for the present studies included those particles passing a U.S. Standard Sieve No. 50 and being retained on a No. 60 sieve; the mean particle diameter for this size range is 0.273 mm.

To eliminate from the experimental systems all extraneous material which might have introduced sources of error and interference, all solutions of the pesticides used in the experimental systems were prepared with twice-distilled water. Cambridge tap water was first distilled in a conventional tin-lined still, and the condensate was transferred into an all-glass still for redistillation. Preliminary boiling with escape of steam was used to purge the water of dissolved carbon dioxide and chlorine prior to collection of the condensate from the redistillation.

EXPERIMENTAL DETAILS

Analytical Methods

Of the substances investigated, only Parathion does not exhibit a characteristic absorption spectrum which is suitable for direct measurement of concentration within the ranges used in the present experiments. Spectra for the six other pesticides are shown in Figures 2-1 through 2-6.

The analytical method employed for Parathion takes advantage of the ease with which the phosphorus-oxygen bond in that material is cleaved by hydroxide. The hydrolysis produces a mole of p-nitrophenol for each mole of Parathion originally present in solution. Because p-nitrophenol has a well-defined absorption spectrum with a high molar absorptivity at the wavelength of maximum adsorption (400 mμ), and because the reaction to form p-nitrophenol from Parathion is rapid and quantitative, the method provides a reliable and sensitive means for analysis of Parathion.

For fairly concentrated samples (1-100μM), about 10 ml of 1 N KOH were added to 50 ml of sample. The mixture was heated to boiling, allowed to cool, diluted to 100 ml, and then the absorbance at 400 mμ was measured in a cell of appropriate length. For more dilute samples, 3 KOH pellets were added to a 100-ml sample, and the procedure outlined above was repeated. The lower limit of the method is about 50 nanomoles/ℓ using a 10-cm cell. The absorption spectrum for p-nitrophenol is shown in Figure 2-7.

After measurement of the absorption spectrum for each solute had been made with a Beckman Model DK-2 spectrophotometer, the absorption maximum for solutions of each of the substances was located precisely with a Beckman Model DU spectrophotometer by measuring intensities of absorption for a localized region on both sides of the wavelength of maximum absorption indicated by the spectra obtained with the Model DK-2. Subsequent spectrophotometric measurements were made with the Model DU.

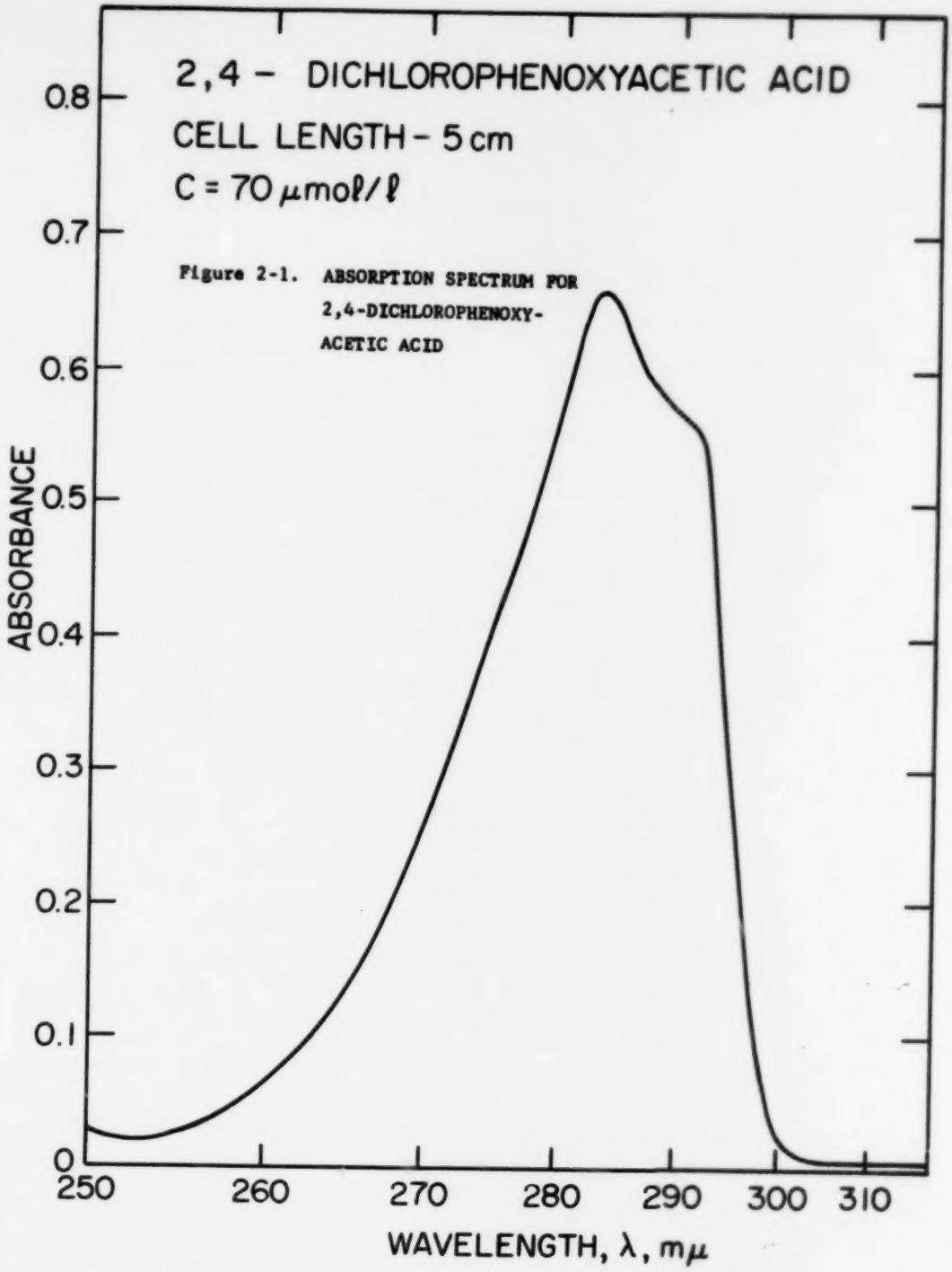

Figure 2-1. ABSORPTION SPECTRUM FOR 2,4-DICHLOROPHENOXY-ACETIC ACID

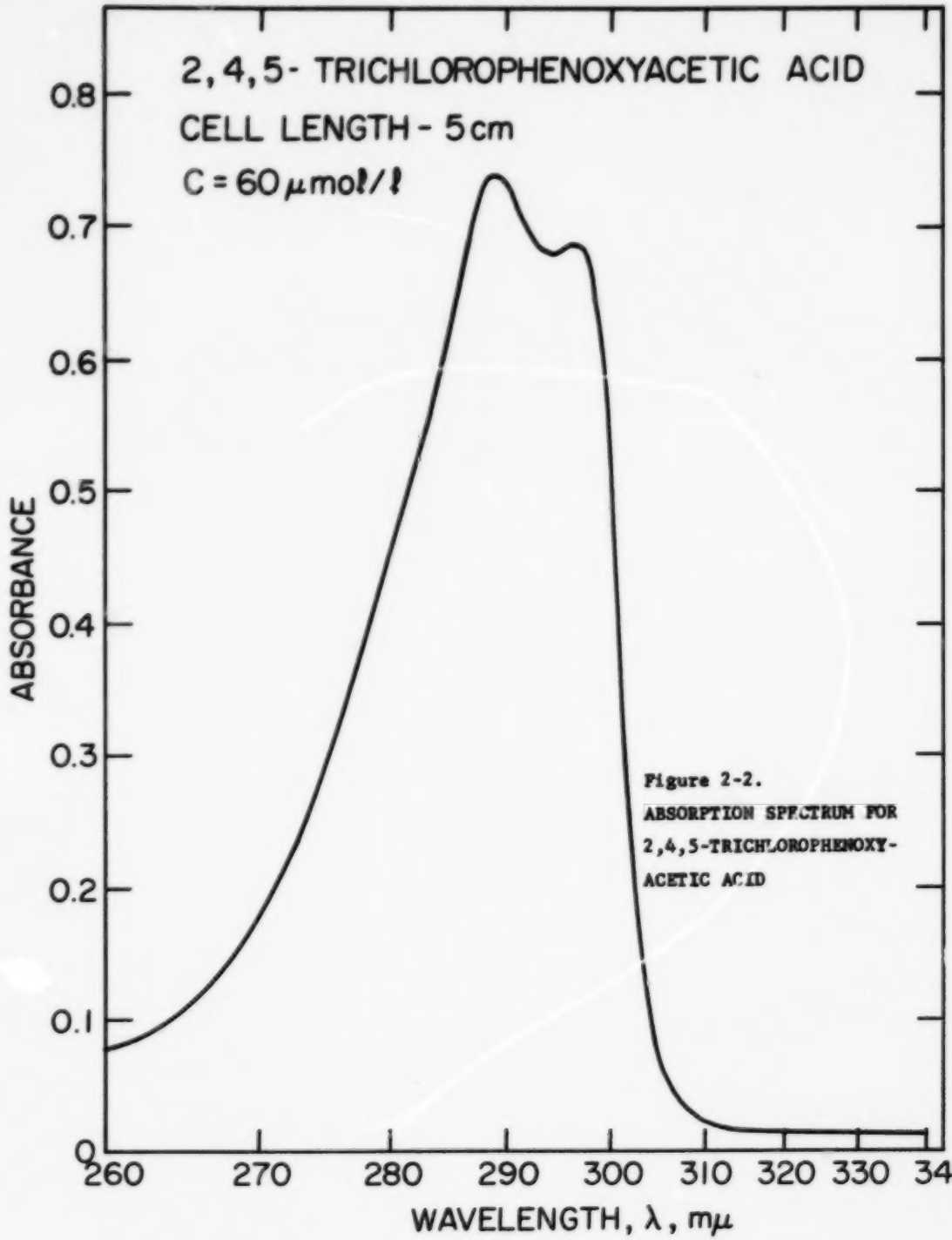

Figure 2-2.
ABSORPTION SPECTRUM FOR 2,4,5-TRICHLOROPHENOXY-ACETIC ACID

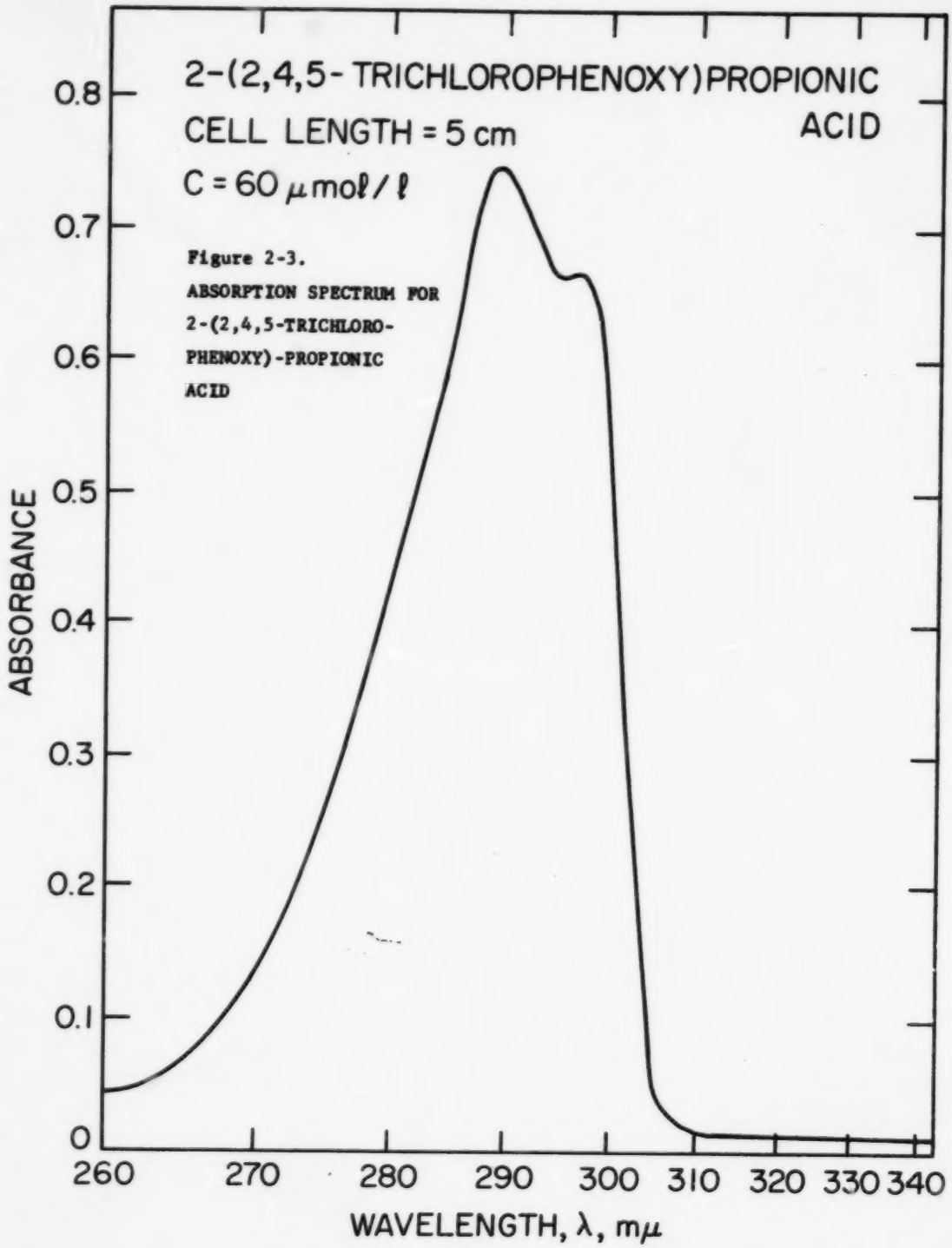

Figure 2-3.
ABSORPTION SPECTRUM FOR 2-(2,4,5-TRICHLORO-PHENOXY)-PROPIONIC ACID

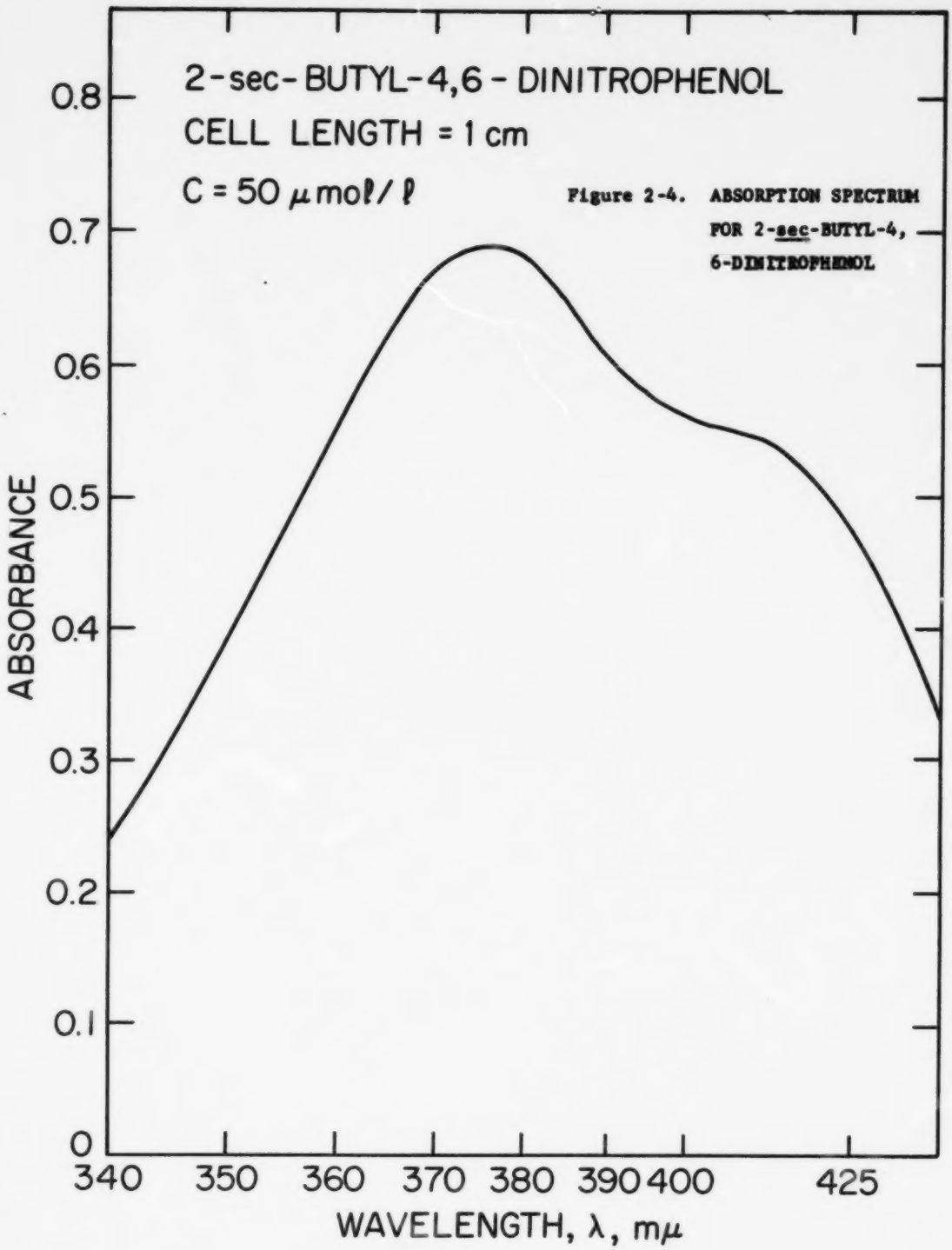

Figure 2-4. ABSORPTION SPECTRUM FOR 2-sec-BUTYL-4, 6-DINITROPHENOL

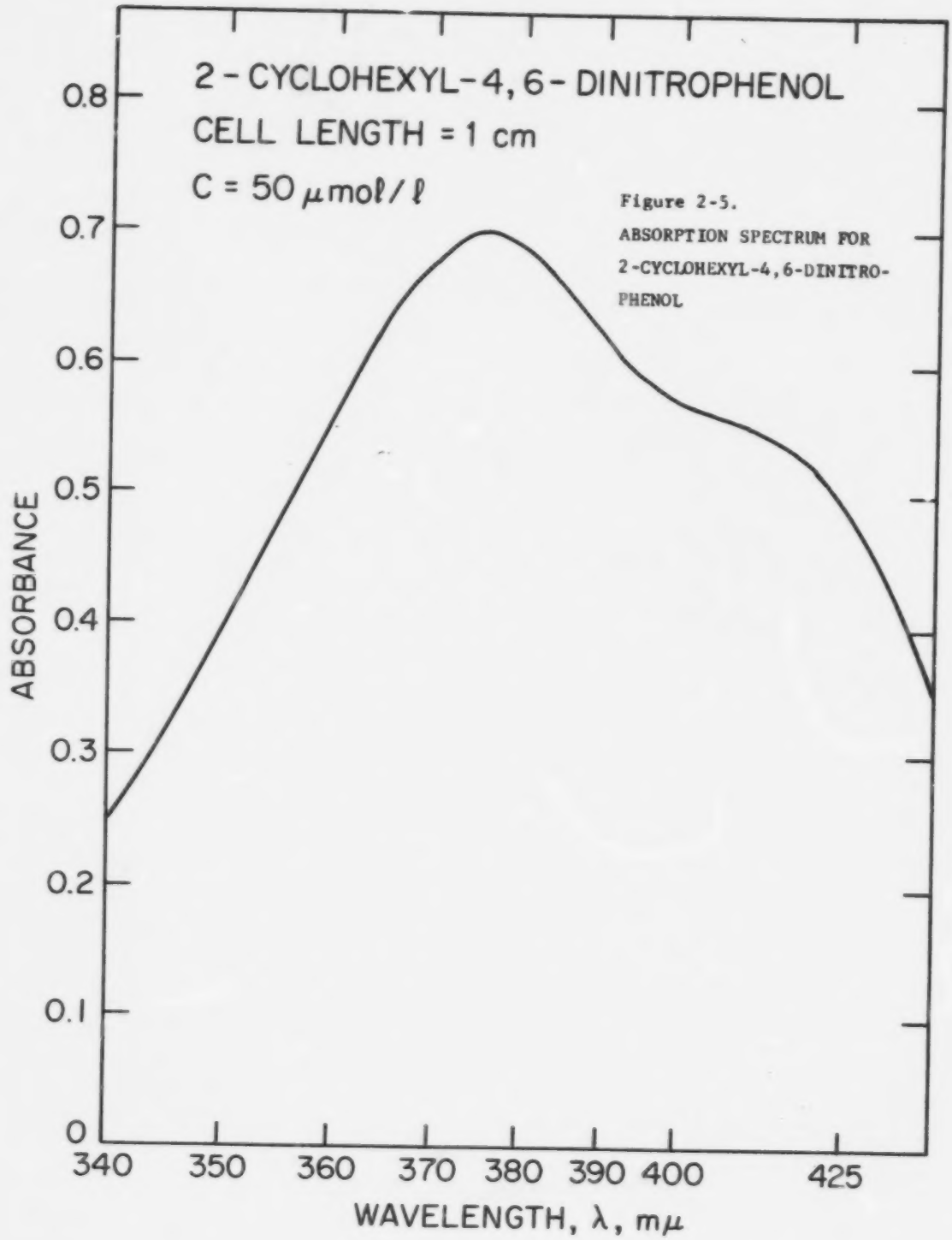

Figure 2-5.
ABSORPTION SPECTRUM FOR
2-CYCLOHEXYL-4,6-DINITRO-
PHENOL

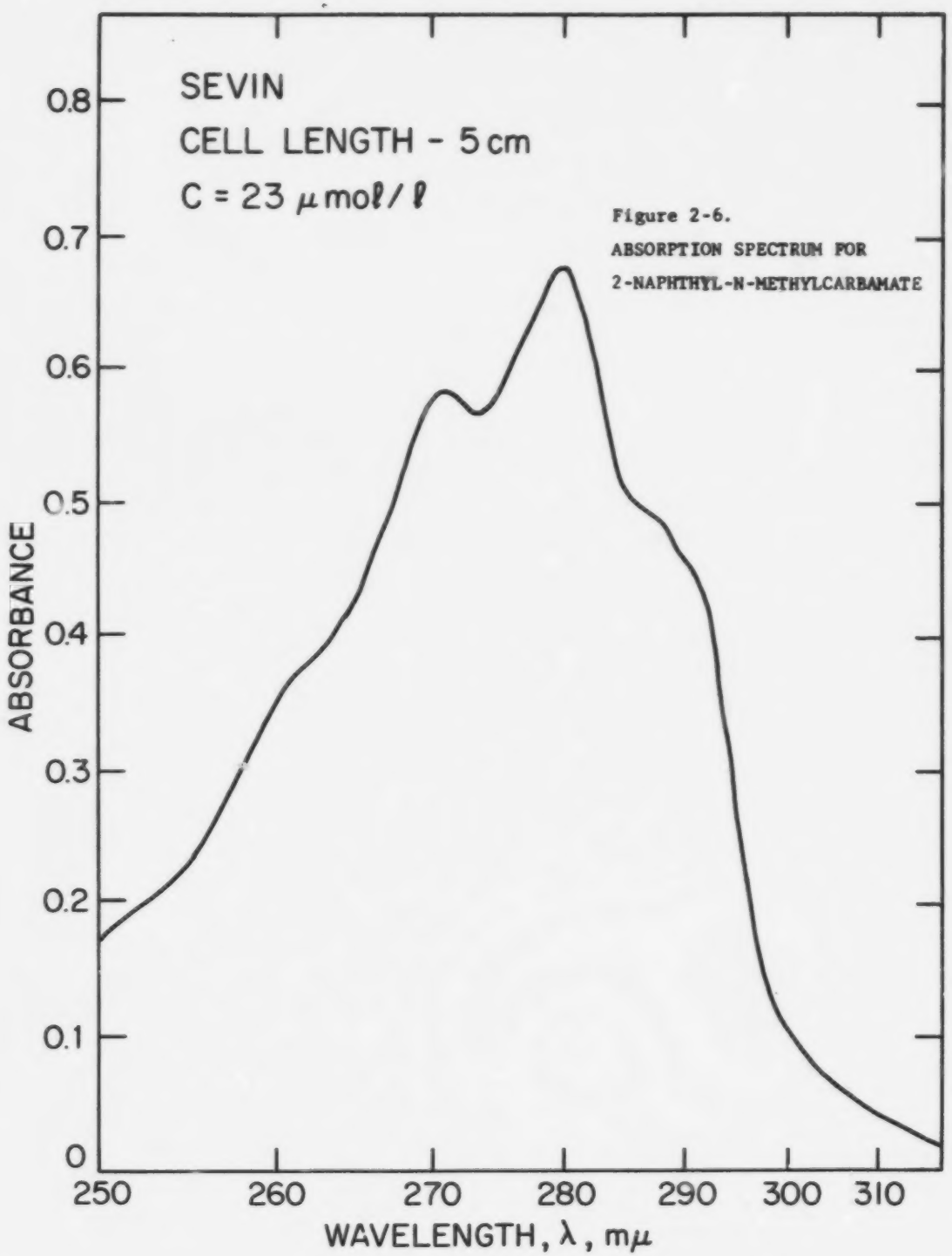

Figure 2-6.
ABSORPTION SPECTRUM FOR
2-NAPHTHYL-N-METHYLCARBAMATE

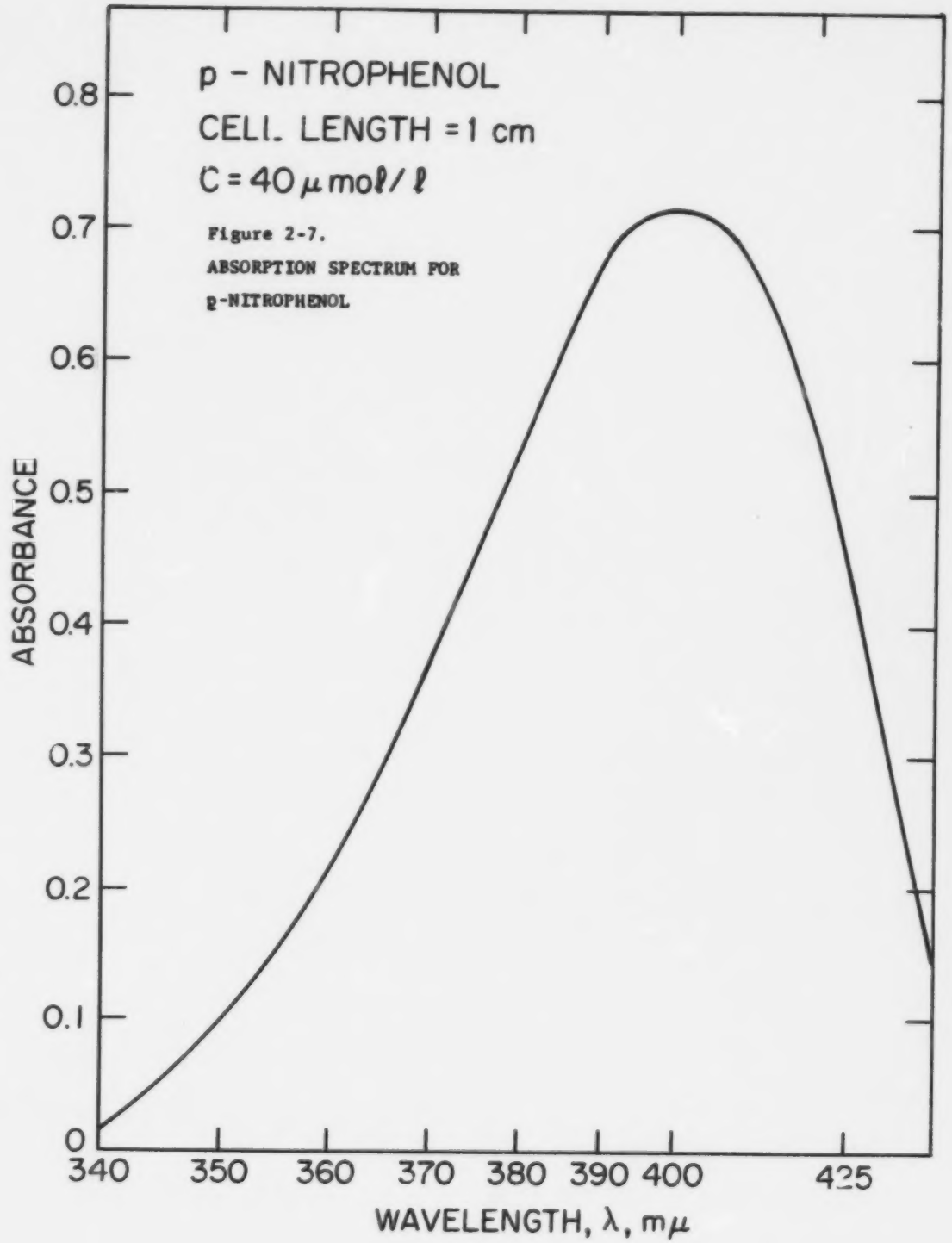

Figure 2-7.
ABSORPTION SPECTRUM FOR
p-NITROPHENOL

Calibration curves for all of the solutes are given in Figures 2-8 through 2-14. Wavelengths of maximum absorption and observed values for the molar absorptivity for each material are listed in Table 2-2.

Table 2-2

Analytical Data for Organic Pesticides

Compound	Wavelength of Maximum Absorption, mμ	Molar Absorptivity, (cm^2/mol) x 10^{-6}
2,4-dichlorophenoxy-acetic acid	284	1.9
2,4,5-trichlorophenoxy-acetic acid	289	2.5
2-(2,4,5-trichloro-phenoxy)propionic acid	289	2.5
2-sec-butyl-4,6-dinitrophenol	375	13.8
2-cyclohyxyl-4,6-dinitrophenol	376	14.0
1-naphthyl-N-methylcarbamate	279	5.9
p-nitrophenol (for Parathion)	400	17.9

Experimental Methods

Agitated non-flow experiments were used in investigating both the kinetics and equilibria of adsorption of the pesticides on carbon. The batch technique was selected because of its relative simplicity. Advantages of this type of system that figured significantly in its selection were its freedom from complex hydraulic parameters indigenous to flow-through systems, its adaptability to small volume work, ease of investigation of variation of conditions, and general facility of operation.

Although column operation seems likely to be used for large-scale technical applications of carbon adsorption to waste treatment, evaluation of the fundamental characteristics of adsorption is simpler with a batch technique. Furthermore, once suitable functional relationships for the variables have been established, extrapolation of data from batch systems to the prediction of behavior in continuous sytems should be feasible.

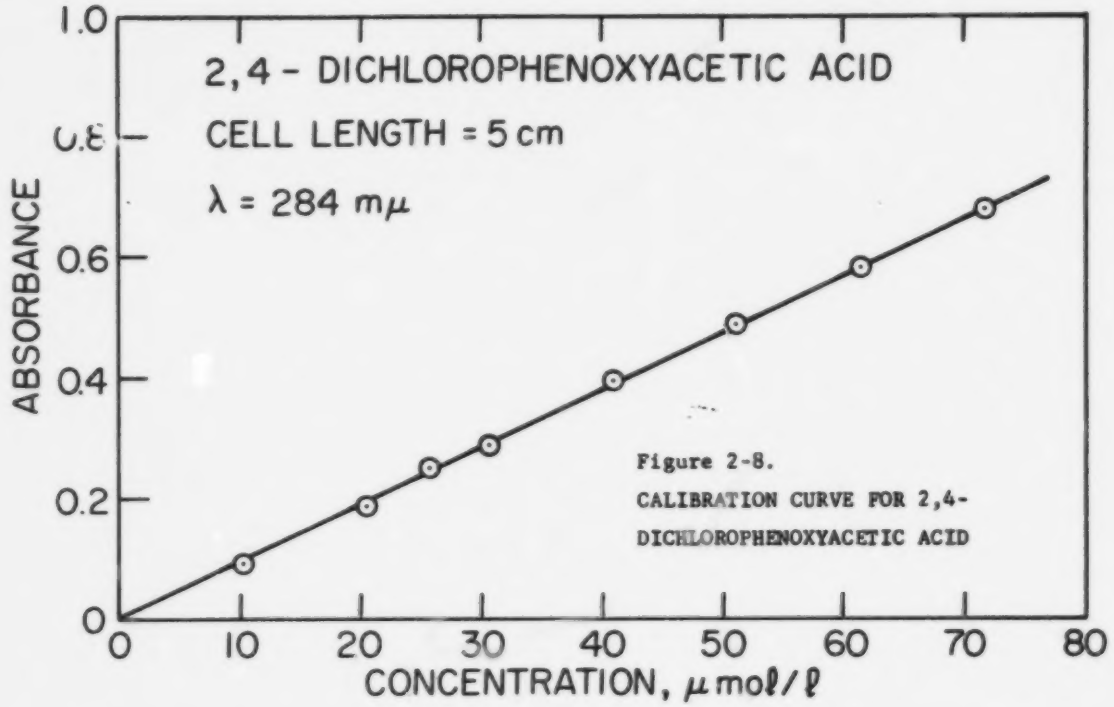

Figure 2-8.
CALIBRATION CURVE FOR 2,4-DICHLOROPHENOXYACETIC ACID

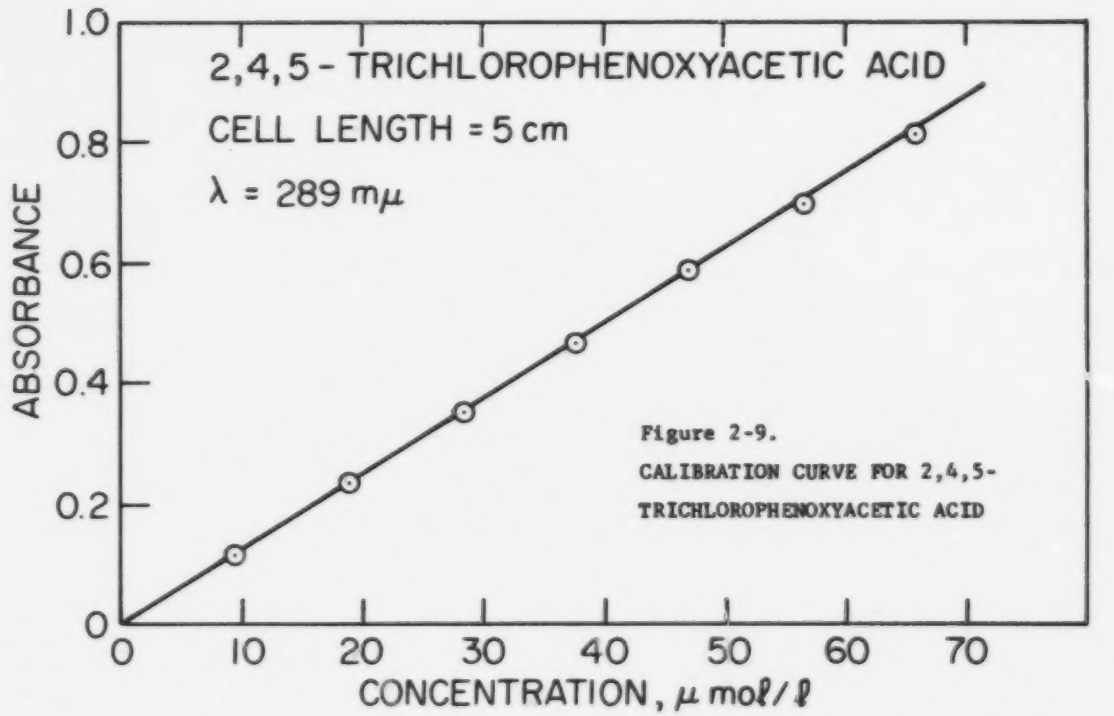

Figure 2-9.
CALIBRATION CURVE FOR 2,4,5-TRICHLOROPHENOXYACETIC ACID

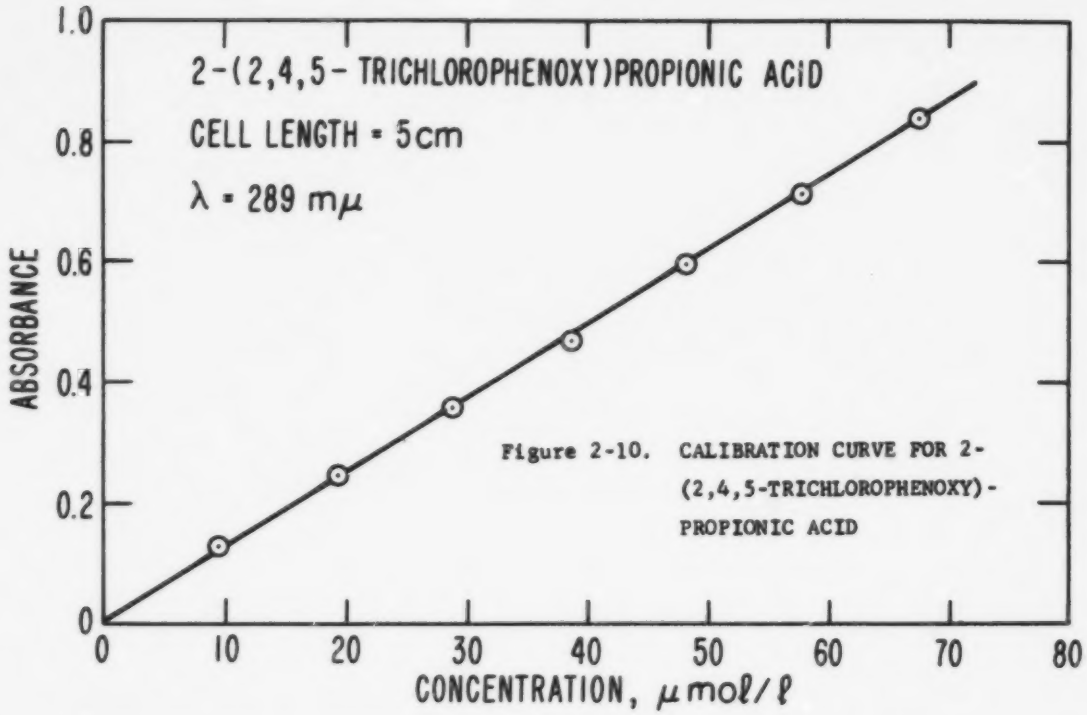

Figure 2-10. CALIBRATION CURVE FOR 2-(2,4,5-TRICHLOROPHENOXY)-PROPIONIC ACID

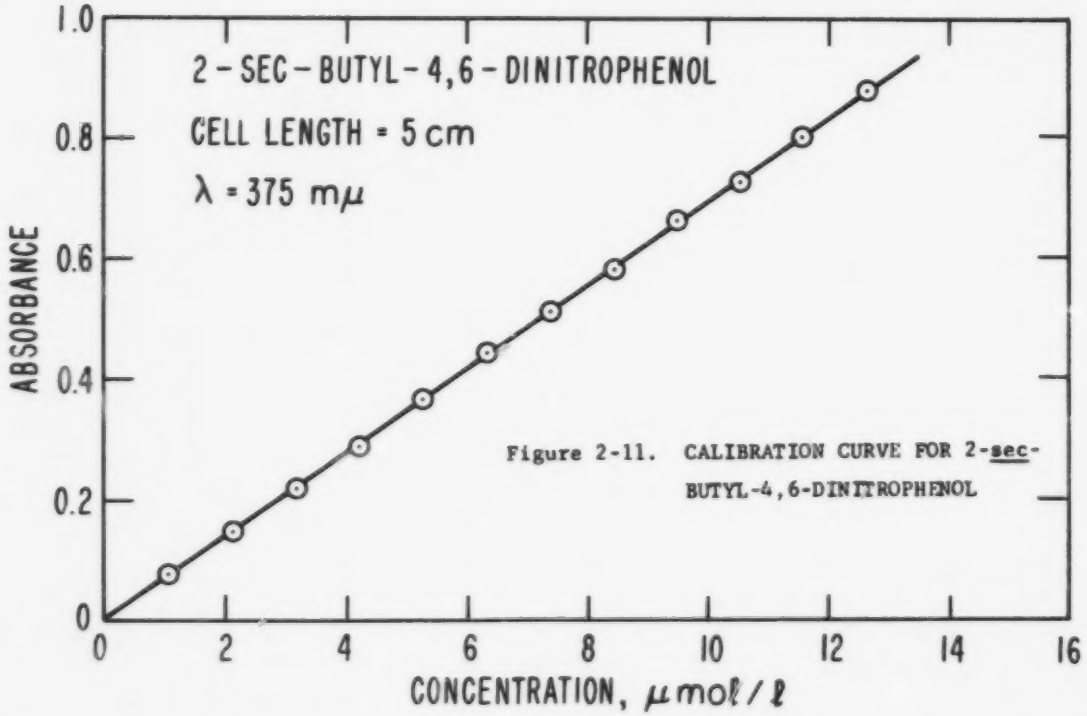

Figure 2-11. CALIBRATION CURVE FOR 2-sec-BUTYL-4,6-DINITROPHENOL

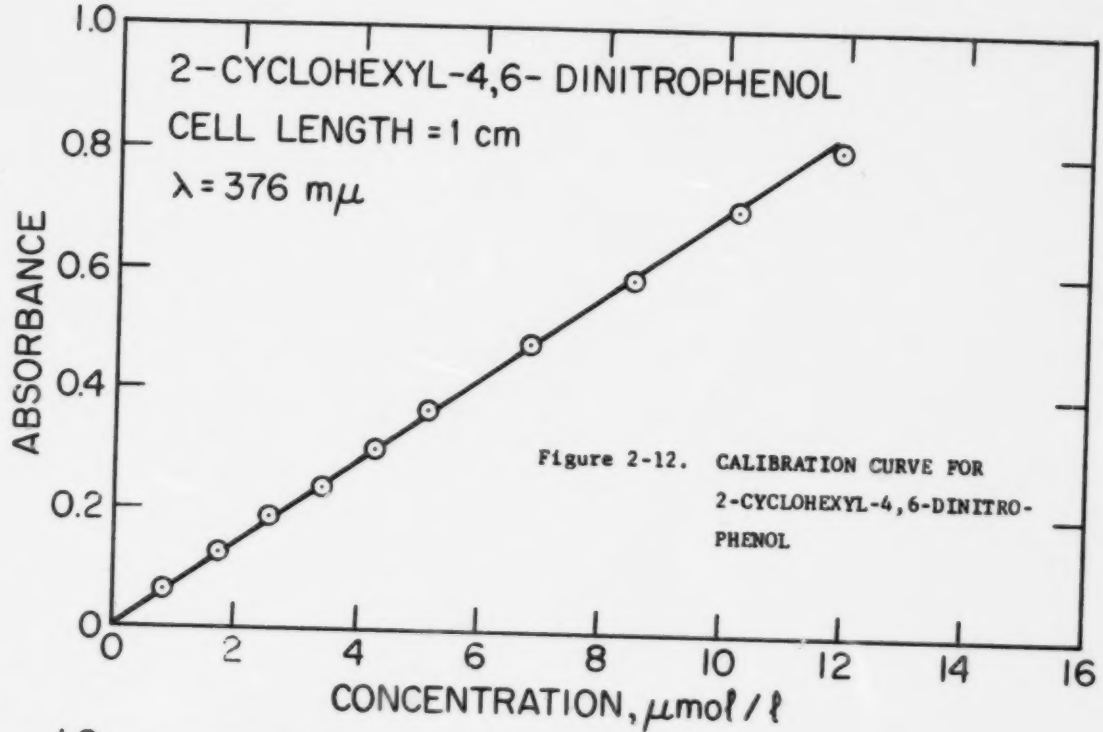

Figure 2-12. CALIBRATION CURVE FOR 2-CYCLOHEXYL-4,6-DINITRO-PHENOL

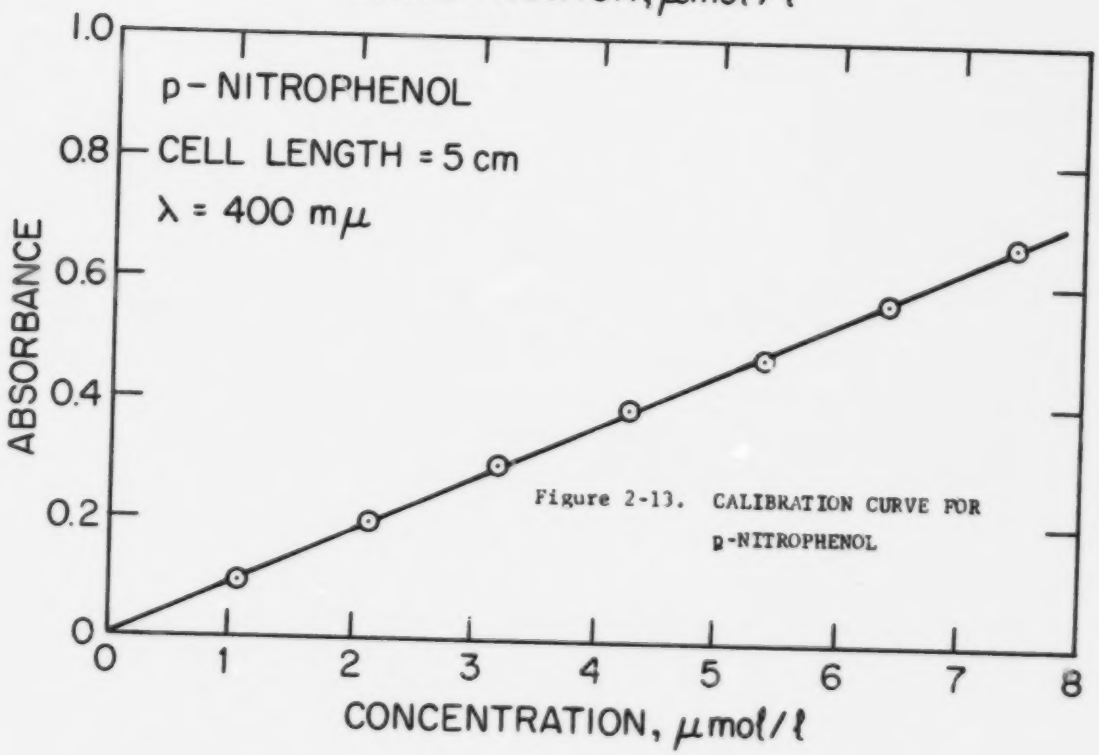

Figure 2-13. CALIBRATION CURVE FOR p-NITROPHENOL

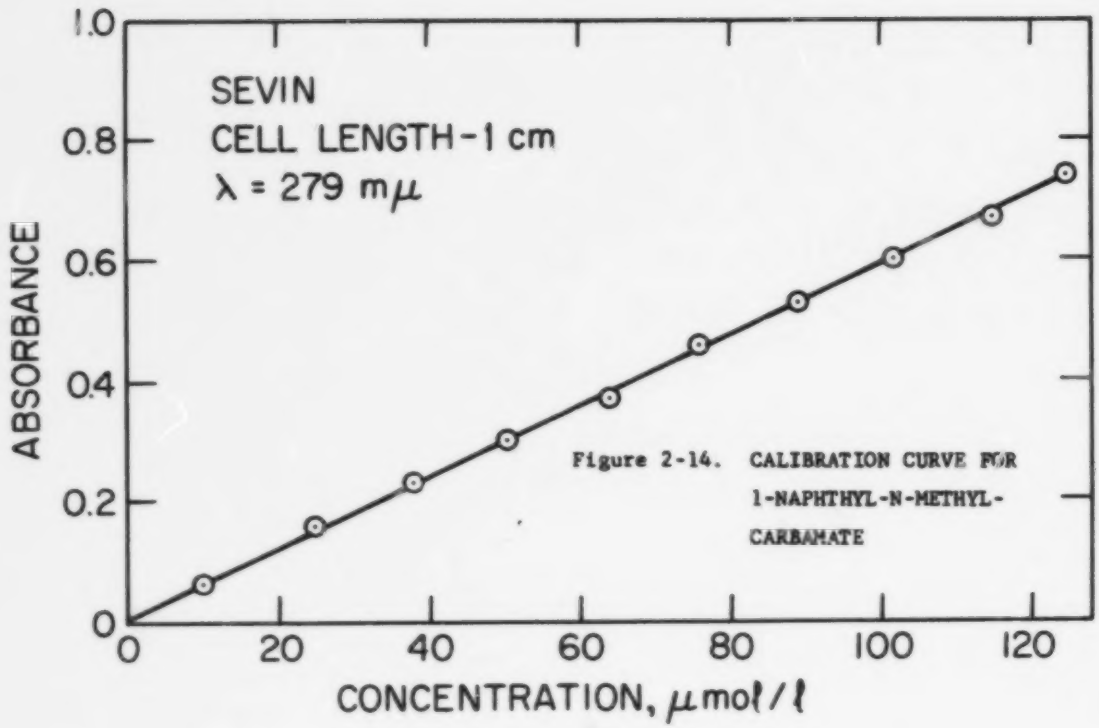

Figure 2-14. CALIBRATION CURVE FOR 1-NAPHTHYL-N-METHYL-CARBAMATE

The reaction vessels for the kinetic studies were 4000-ml resistant-glass bottles, in which solutions were agitated with Teflon-coated stirring rods extending directly into the adsorbate solution and connected to synchronous motors operating at 1550 rpm. Previous kinetic studies in similar systems had shown that the rate of adsorption was independent of stirring rate at rotations greater than a few hundred revolutions per minute.[2] Temperature control for the rate studies was maintained by immersing the reaction vessels in water baths, thermoregulated to 0.5°C. All kinetic studies have been conducted at 28°C.

For each experiment on rate of adsorption, an 8-liter volume of adsorbate solution was prepared at a concentration slightly higher than that desired for the kinetic experiment. Spectrophotometric measurement of the exact concentration of solute in the solution was then made, and the original 8-liter volume diluted appropriately to give more closely a solution of the desired concentration. Exactly 3000 ml of the adjusted solution was then placed in each of two 4-liter reaction vessels. The reaction vessels were then placed in a water-bath for approximately 24 hours to allow the solution to attain the desired temperature and to reach adsorptive equilibrium with the surfaces of the vessels. Prior to introduction of a suitable, accurately weighed quantity of carbon to each vessel, an initial sample was removed and analyzed for concentration of adsorbate. This gave an accurate check on the preparation of the solution and served as the reference concentration for the rate study. The carbon was then introduced into the vessel and was rapidly dispersed by the motor-driven stirrer operating at 1550 rpm. At appropriate intervals the stirring was briefly interrupted while samples of the supernatant solution were pipetted from each of the reaction vessels; the samples for analysis resulted in some small decrease in total adsorbate available to the adsorbent, but the cumulative error of 2% to 3% was not significant for this type of experiment. The running of two parallel experiments, which were identical in all details, provided a check on the reproducibility of the data.

For investigation of adsorptive capacities and equilibria, large volumes of adsorbate solution were prepared and 250-ml measures of this solution were dispensed into 300-ml resistant-glass reaction flasks. A suitable, accurately weighed amount of adsorbent was then added to each flask, the weight being varied so as to cover the range of equilibrium solute concentrations of interest. For each study, several flasks of solution were left without carbon for use as blanks. The ground-glass-stoppered reaction flasks were then sealed and placed in an oscillating shaker to be shaken for approximately 2 weeks, the times required for equilibrium to be obtained having been determined previously for each type of system. Samples from each of the solutions were analyzed at the end of the appropriate period; the amount of adsorption was computed from the difference between the concentration of adsorbate measured for the blanks and for each reacted solution. Most studies were conducted in a room that was maintained at a reasonably uniform temperature, so that fluctuations in the temperatures of the solutions were no more than 2 to 3°C over the duration of the study. The mean temperature for the equilibrium studies was 25°C.

RATES OF ADSORPTION

Previous investigations have indicated that the rate-limiting step for removal of organic solutes from dilute aqueous solution by porous activated carbon in agitated non-flow systems is one of intraparticle transport of the solute in the pores and capillaries of the adsorbent.[2] For systems in which intraparticle transport is the rate-limiting step, data for uptake of solute from solution should give a linear plot as a function of the square-root of time from introduction of the adsorbent to the system.[3] In accord with this method for representing data for systems in which intraparticle transport is the rate-limiting mechanism, the data for the present experiments have been plotted as a function of the square-root of time.

The rate data for the experiments on adsorption of the pesticides on activated carbon are plotted in Figures 2-15 through 2-21. The $(C_o-C)/m$ values in these plots represent the amount of solute, both in micromoles and milligrams, removed from solution per gram of carbon. Good linearization of the data is observed for the experiments, in accord with expected behavior for intraparticle-transport rate control. The linear traces facilitate comparison of relative rates of adsorption of the organic pesticides, and such comparison is made in Table 2-3 using the square of the slope of each plot as the relative rate constant for the experiment.

Table 2-3

Relative Rate Constants for Adsorption of Organic Pesticides on Carbon

28°C, 25 mg/l 0.273-mm Columbia Carbon, C_o = 10μmol/ℓ

Compound	Relative Rate Constant, k, $[(\mu mol/g)^2/hr] \times 10^{-4}$
2,4-dichlorophenoxyacetic acid	1.44
2,4,5-trichlorophenoxyacetic qcid	1.00
2-(2,4,5-trichlorophenoxy)propionic acid	0.71
2-sec-butyl-4,6-dinitrophenol	1.35
2-cyclohexyl-4,6-dinitrophenol	1.12
1-naphthyl N-methylcarbamate	1.64
0,0-diethyl-0-p-nitrophenylphosphorothioate	1.49

It is of interest that the rate constants for adsorption of the various organic pesticides on the 0.273-mm carbon are remarkably similar. The data suggest that, even for a rather broad spectrum of different types of organic pesticides, similar rates of removal from solution should obtain. Thus, the effectiveness of activated carbon as related to rate of removal of organic pesticides from solution should be relatively independent of the type of organic pesticide, at least within the classes of compounds and conditions used for the present experiments.

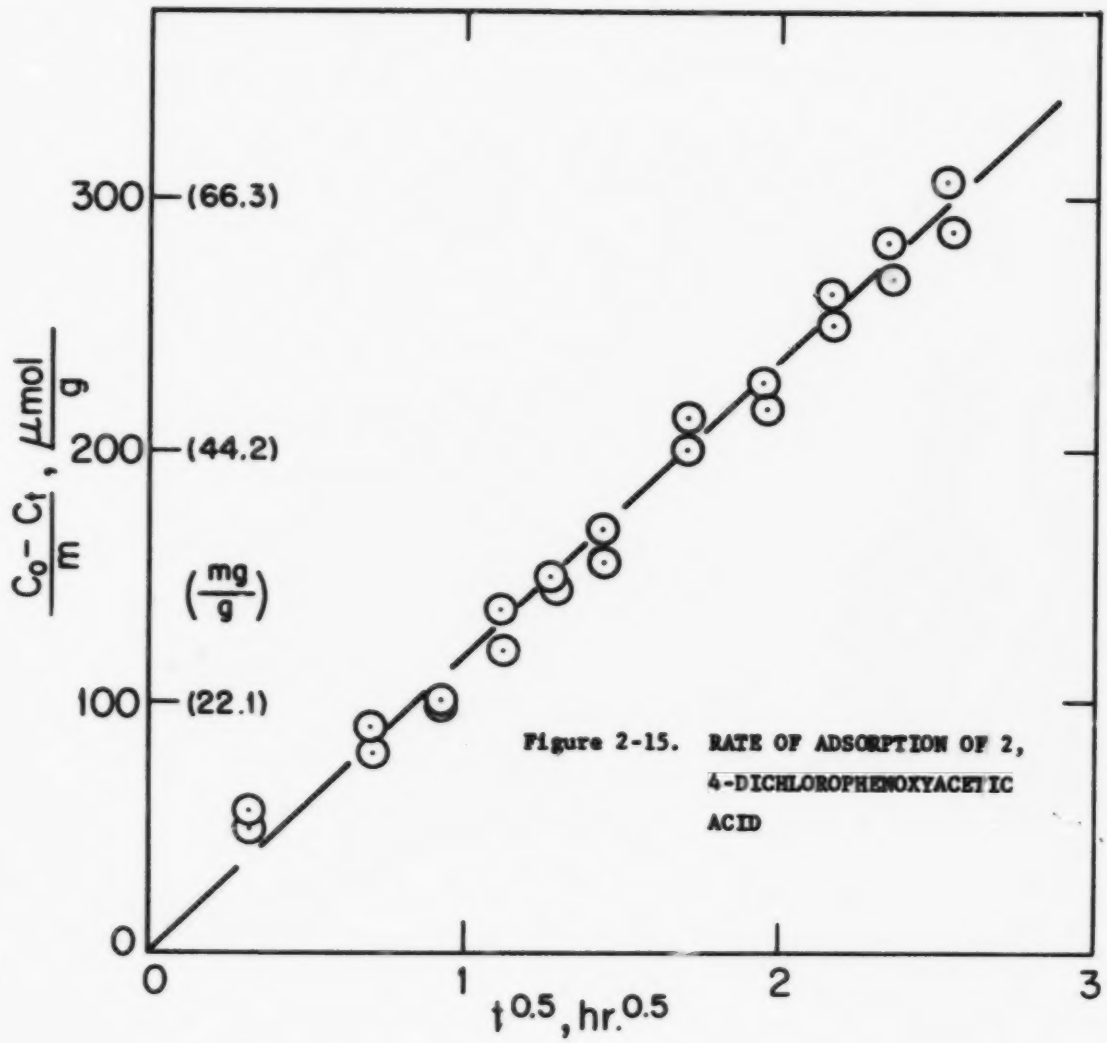

Figure 2-15. RATE OF ADSORPTION OF 2, 4-DICHLOROPHENOXYACETIC ACID

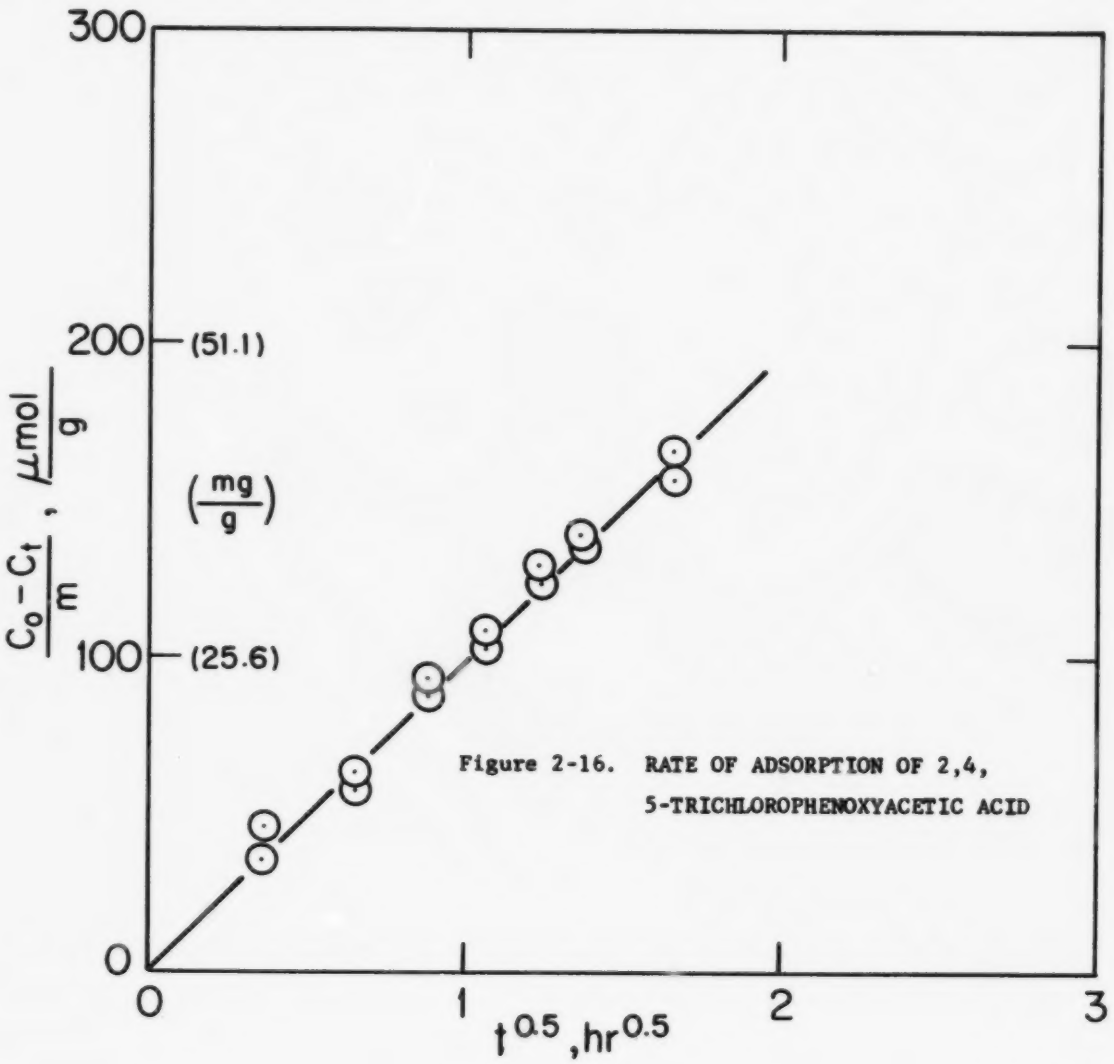

Figure 2-16. RATE OF ADSORPTION OF 2,4, 5-TRICHLOROPHENOXYACETIC ACID

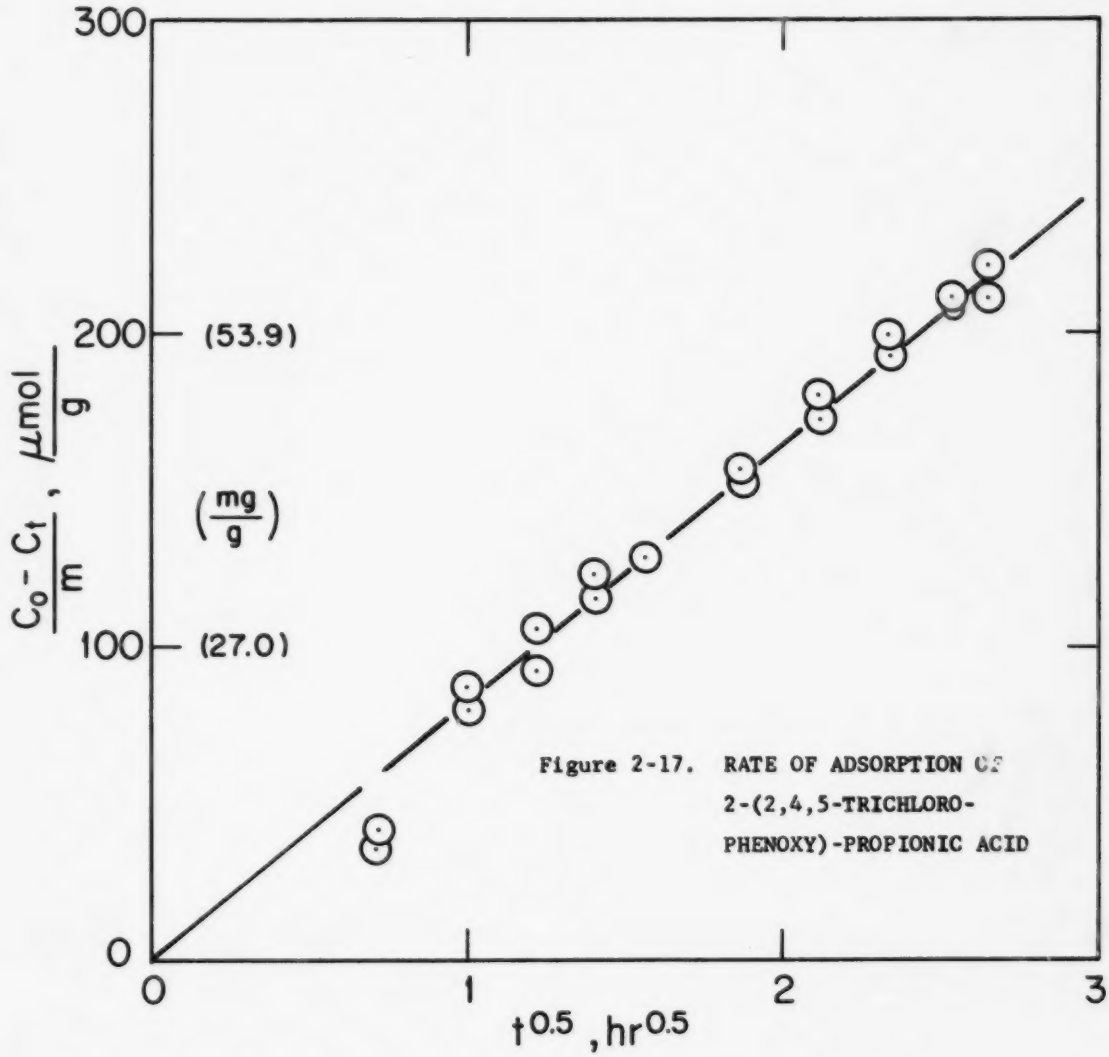

Figure 2-17. RATE OF ADSORPTION OF 2-(2,4,5-TRICHLORO-PHENOXY)-PROPIONIC ACID

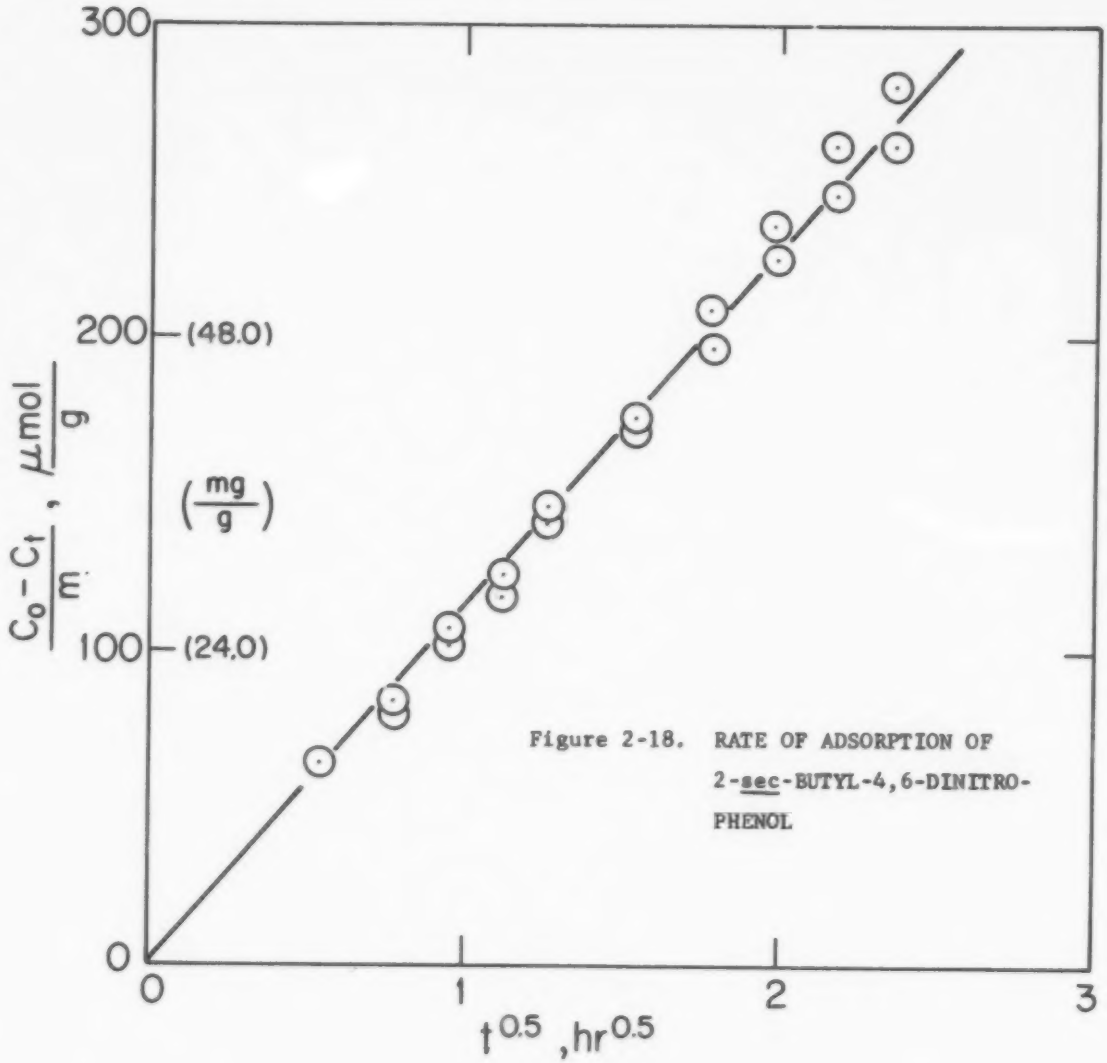

Figure 2-18. RATE OF ADSORPTION OF 2-sec-BUTYL-4,6-DINITRO-PHENOL

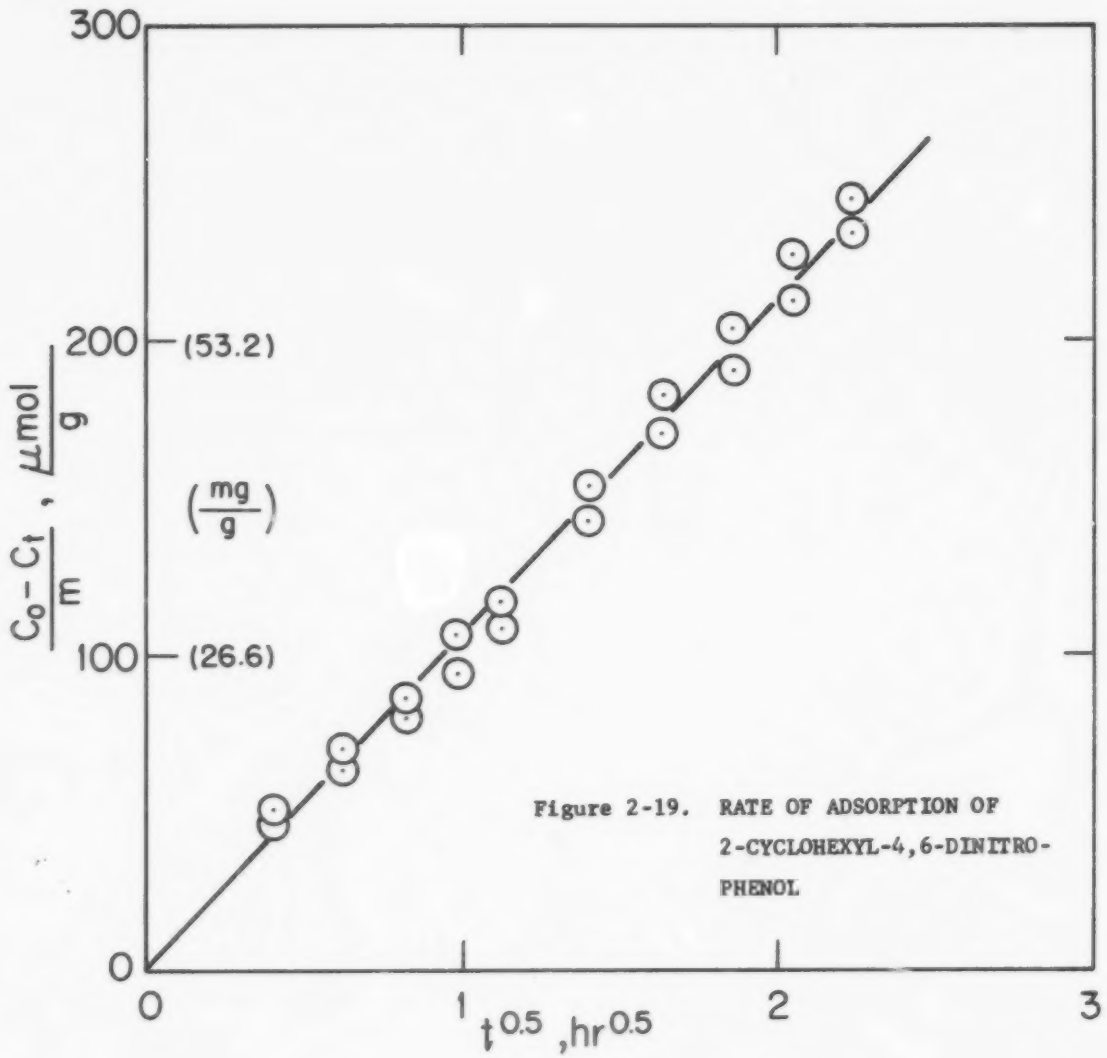

Figure 2-19. RATE OF ADSORPTION OF 2-CYCLOHEXYL-4,6-DINITRO-PHENOL

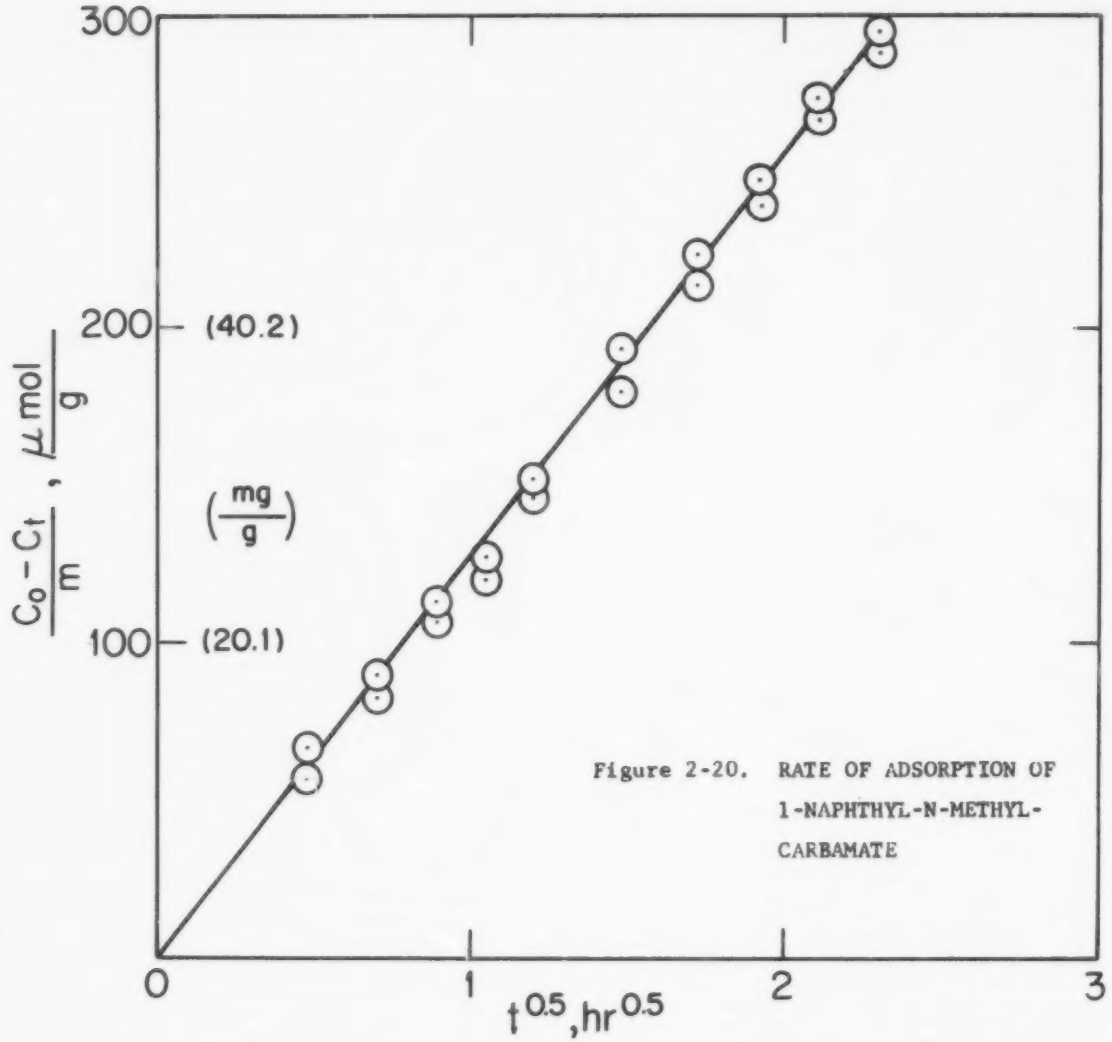

Figure 2-20. RATE OF ADSORPTION OF 1-NAPHTHYL-N-METHYL-CARBAMATE

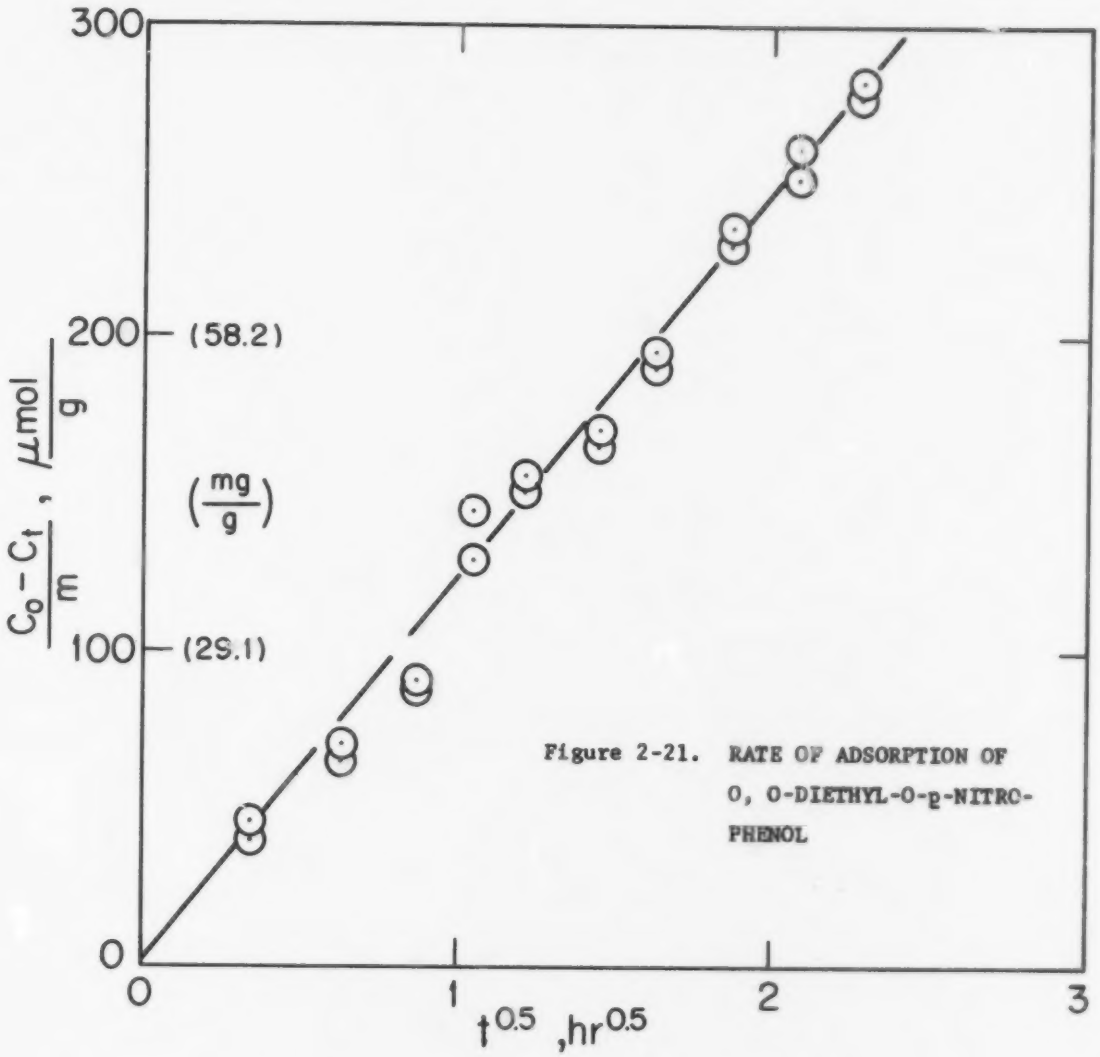

Figure 2-21. RATE OF ADSORPTION OF O, O-DIETHYL-O-p-NITROPHENOL

Concentration of solute in solution was noted to have a significant effect upon the rate of removal by activated carbon. The data shown in Figures 2-15 through 2-21 are for experiments conducted with a solution containing initially about 10 micromoles of solute per liter. Figure 2-22 shows some data for experiments conducted with some of the pesticides at concentrations greater than and slightly smaller than 10 micromoles per liter. The uppermost curve in Figure 2-22 is for adsorption of 2,4-dichlorophenoxyacetic acid from a solution having an initial concentration of 52.2 micromoles per liter. The middle curve in Figure 2-22 is for 2-(2,4,5-trichlorophenoxy)propionic acid in a solution having an initial concentration of 45.2 micromoles per liter, and the lower curve in Figure 2-22 is for adsorption of 2-cyclohexyl-4,6-dinitrophenol from a solution with an initial concentration of 7.7 micormoles per liter.

For the 2,4-dichlorophenoxyacetic acid the increase by a factor of 5.1 in the initial molar concentration, over that used in the experiment represented by the data in Figure 2-15, resulted in a new rate constant of $16.0 \times 10^4 (\text{micromoles/g})^2/\text{hr}$ as compared to a relative rate constant of $1.44 \times 10^4 (\text{micromoles/g})^2/\text{hr}$ for the experiment in which the initial concentration was 10.3 micromoles/1. The experiment at high concentration with 2-(2,4,5-trichlorophenoxy)propionic acid, which represented an increase in initial molar concentration by a factor of 4.6 times that used for the experiment represented by the data in Figure 2-17, yielded a new relative rate constant of $7.56 \times 10^4 (\text{micromoles/g})^2/\text{hr}$ as compared to a value of $0.71 \times 10^4 (\text{micromoles/g})^2/\text{hr}$ for the experiment with an initial molar concentration of 9.8 micromoles/1.

It is interesting to note that the ratio of the relative rate constants for the two solutes, 2,4-dichlorophenoxyacetic acid and 2-(2,4,5-trichlorophenoxy)propionic acid, obtained from the experiments at low concentration is 2.03, while the ratio of the relative rate constants obtained from the experiments at the high concentrations is 2.11. Thus, it appears that the effect of initial concentration upon the rate at which organic pesticides are removed

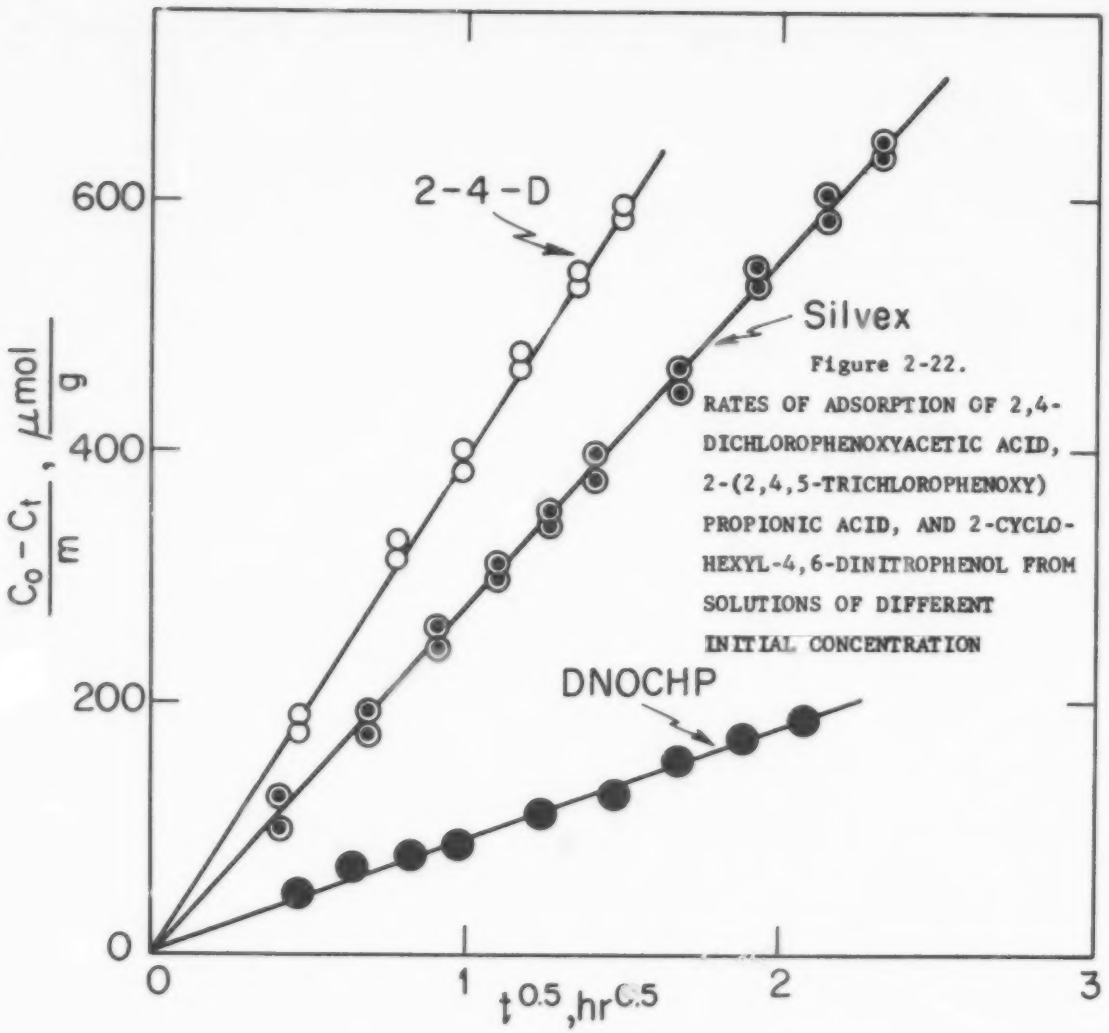

Figure 2-22.
RATES OF ADSORPTION OF 2,4-DICHLOROPHENOXYACETIC ACID, 2-(2,4,5-TRICHLOROPHENOXY) PROPIONIC ACID, AND 2-CYCLOHEXYL-4,6-DINITROPHENOL FROM SOLUTIONS OF DIFFERENT INITIAL CONCENTRATION

from water by activated carbon is relatively uniform, at least for similar classes of organic pesticides.

The relative rate constant for the 2-cyclohexyl-4,6-dinitrophenol obtained from the experiment with an initial molar concentration of 7.7 micromoles/l was 0.90×10^4(micromoles/g)^2/hr as compared to a value of 1.12×10^4(micromoles/g)^2/hr obtained for the experiment with an initial molar concentration of 10.2 micromoles/l. Thus the effect of initial concentration appears qualitatively uniform for different classes of organic pesticides.

ADSORPTION EQUILIBRIA

The extent to which the full surface area of an activated carbon can be used for adsorption depends on the concentration of solute in the solution with which the carbon is mixed. The specific relationship between concentration of solute and the degree of its removal from solution by an adsorbent at constant temperature and for conditions of equilibrium defines the adsorption isotherm. The preferred form for representing the adsorption isotherm is to express the quantity of solute adsorbed per unit weight of adsorbent as a function of C, the equilibrium concentration of solute remaining in solution.

A number of different types of adsorption relationships may obtain under different circumstances. The most common relationship between the amount of solute adsorbed per unit of adsorbent and the equilibrium concentration in solution is obtained for systems in which it appears that adsorption from solution leads to the deposition of only a single layer of solute molecules on the surface of the solid. This type of adsorption equilibrium is best represented by the Langmuir model for adsorption, which assumes that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no movement of adsorbate molecules in the plane of the surface after initial adsorption.[4]

The form of the Langmuir adsorption isotherm is

$$X = \frac{X_m bC}{1 + bC} \quad \text{.....(2-1)}$$

in which C indicates the measured concentration in solution at equilibrium, X_m is equal to the number of moles of solute per gram of carbon adsorbed in forming a complete monolayer on the carbon surface, X represents the number of moles of solute adsorbed per gram of carbon at concentration C, and b denotes a constant related to the energy of adsorption. The reciprocal, 1/b, is the concentration at which adsorption attains half its limiting X_m value.

Two convenient linear forms for the Langmuir equation are[5]:

$$\frac{1}{X} = \frac{1}{X_m} + \frac{1}{bX_m C} \quad \text{.....(2-2)}$$

and

$$\frac{C}{X} = \frac{1}{bX_m} + \frac{C}{X_m} \quad \text{.....(2-3)}$$

Either Equation 2-2 or Equation 2-3 may be used for linearization of data that conform to the Langmuir equation. The form chosen usually depends on the range and spread of the data and on the particular range of data to be emphasized.

All of the organic pesticides tested exhibit equilibrium adsorption on the experimental carbon in reasonable accord with the Langmuir model for adsorption. The data for isothermal equilibrium adsorption experiments are plotted in Figures 2-23 through 2-28. The points on these plots are the experimental data; the solid curves through the points are calculated Langmuir adsorption isotherms. Figures 2-29 through 2-34 are linear plots of the data

according to the linear form of the Langmuir adsorption isotherm given by Equation 2-2. The intercept, with the ordinate, of each line drawn through the data in Figures 2-29 through 2-34 represents the reciprocal of the ultimate capacity for adsorption, $\frac{1}{X_m}$, and the slope of each plot represents the reciprocal of bX_m. From the intercepts and slopes of the linear Langmuir plots, values for the Langmuir constants for each solute have been calculated; these values for the Langmuir parameters are listed in Table 2-4.

Table 2-4

Langmuir Constants for Adsorption Isotherms of Pesticides on Activated Carbon

25°C, 0.273-mm Columbia LC carbon

Compound	X_m, (μmol/g)x 10^{-3}	b, (1/μmol)
2,4-dichlorophenoxyacetic acid	1.75	0.095
2,4,5-trichlorophenoxyacetic acid	1.75	0.150
2-(2,4,5-trichlorophenoxy)propionic acid	1.72	0.145
2-sec-butyl-4,6-dinitrophenol	1.85	0.174
2-cyclohexyl-4,6-dinitrophenol	1.88	0.148
O,O-diethyl-O-p-nitrophenyl phosphorothiate	1.82	1.22

As was the case for the relative rate constants for the different organic pesticides, values of X_m, listed in Table 2-4, are quite similar in magnitude for the different adsorbates, on the order of 1800 micromoles of solute per gram of carbon. Thus, the ultimate capacity appears to be relatively independent of the type of organic pesticide tested, at least within the experimental ranges. With the exception of the parathion, values for the parameter b, which is a measure of the energy of adsorption, are quite similar for the organic pesticides. The fact that the value for b for the parathion is an order of magnitude higher than values of b for the other organic

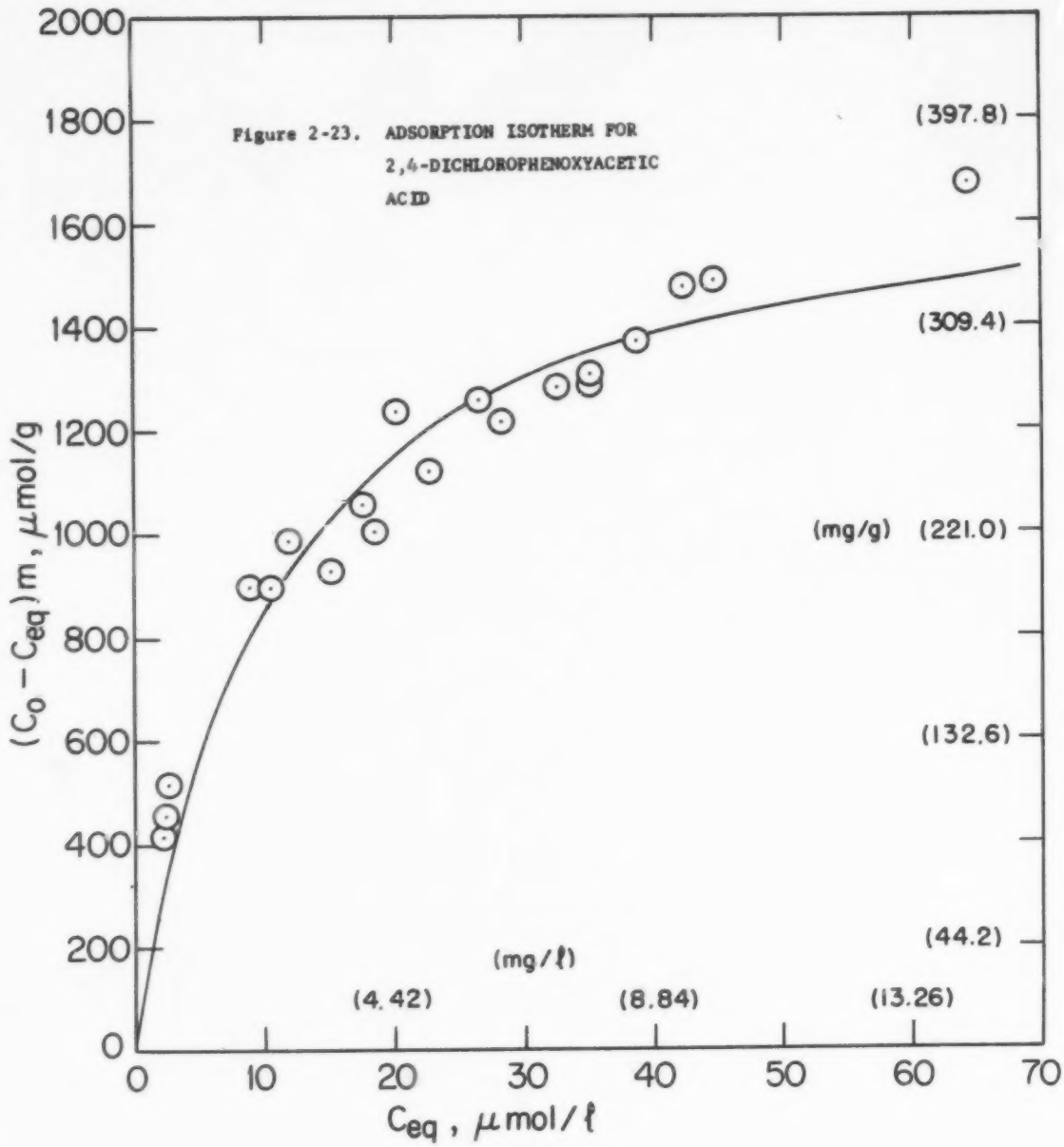

Figure 2-23. ADSORPTION ISOTHERM FOR 2,4-DICHLOROPHENOXYACETIC ACID

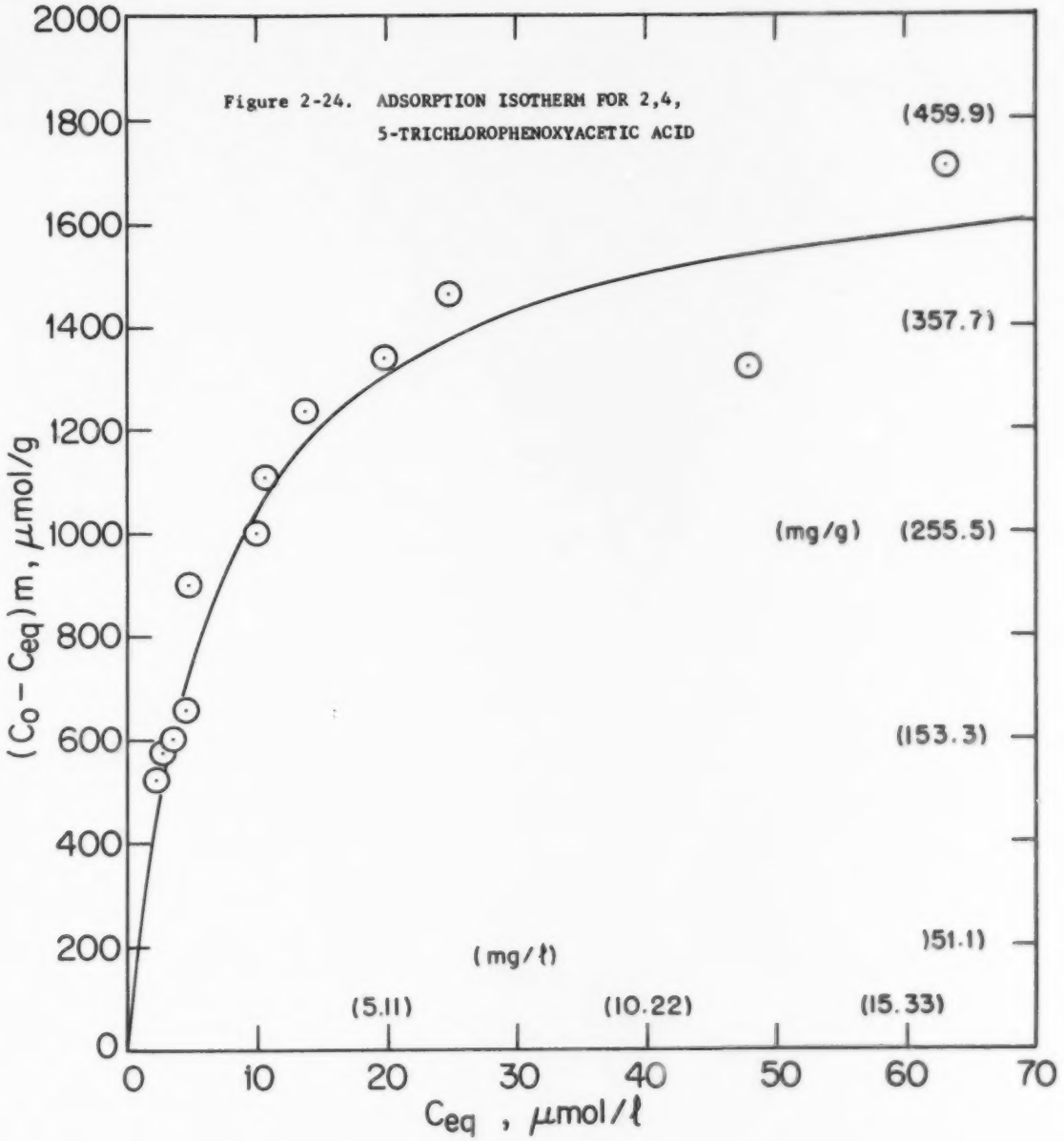

Figure 2-24. ADSORPTION ISOTHERM FOR 2,4, 5-TRICHLOROPHENOXYACETIC ACID

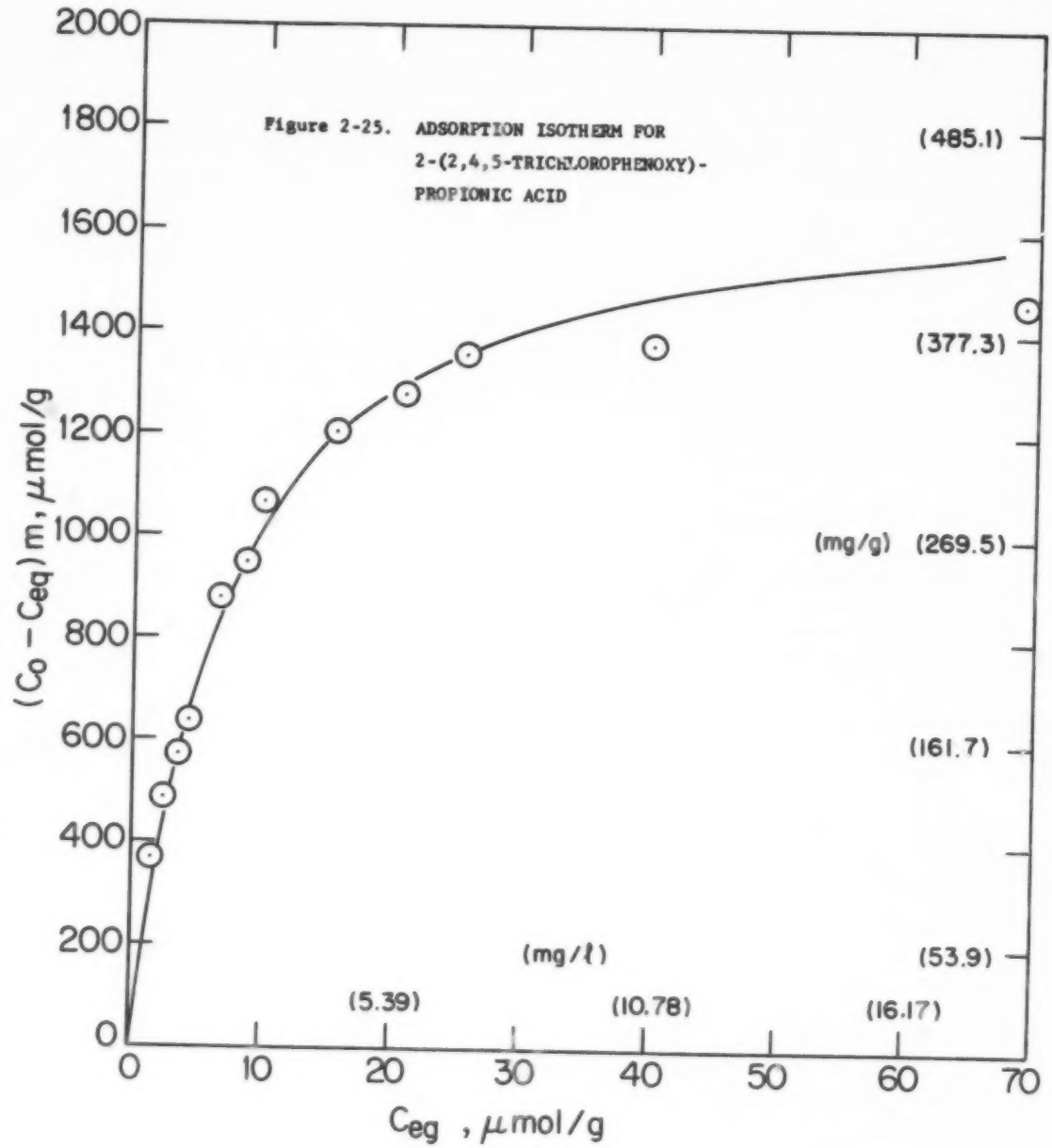

Figure 2-25. ADSORPTION ISOTHERM FOR 2-(2,4,5-TRICHLOROPHENOXY)-PROPIONIC ACID

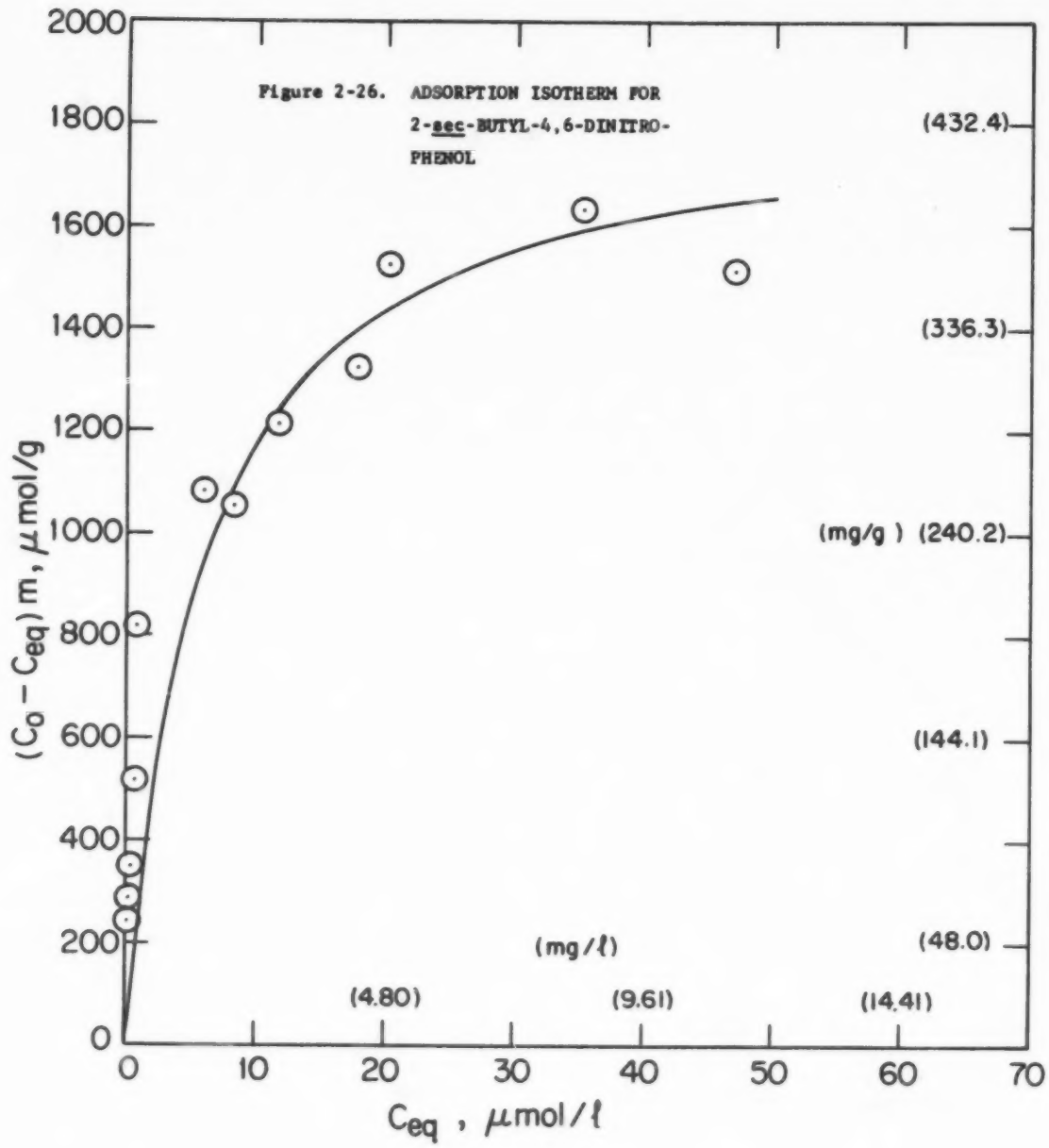

Figure 2-26. ADSORPTION ISOTHERM FOR 2-sec-BUTYL-4,6-DINITRO-PHENOL

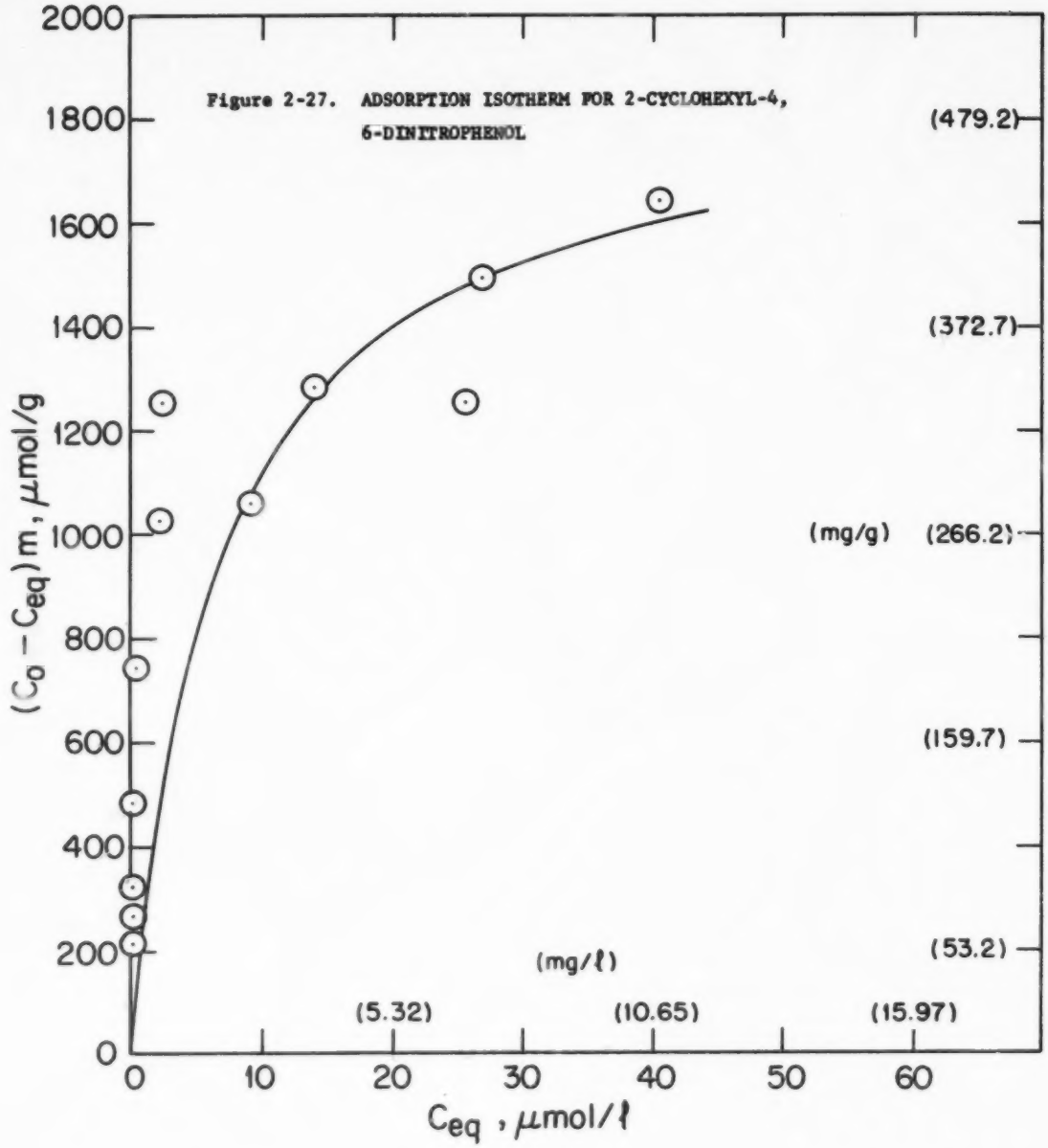

Figure 2-27. ADSORPTION ISOTHERM FOR 2-CYCLOHEXYL-4, 6-DINITROPHENOL

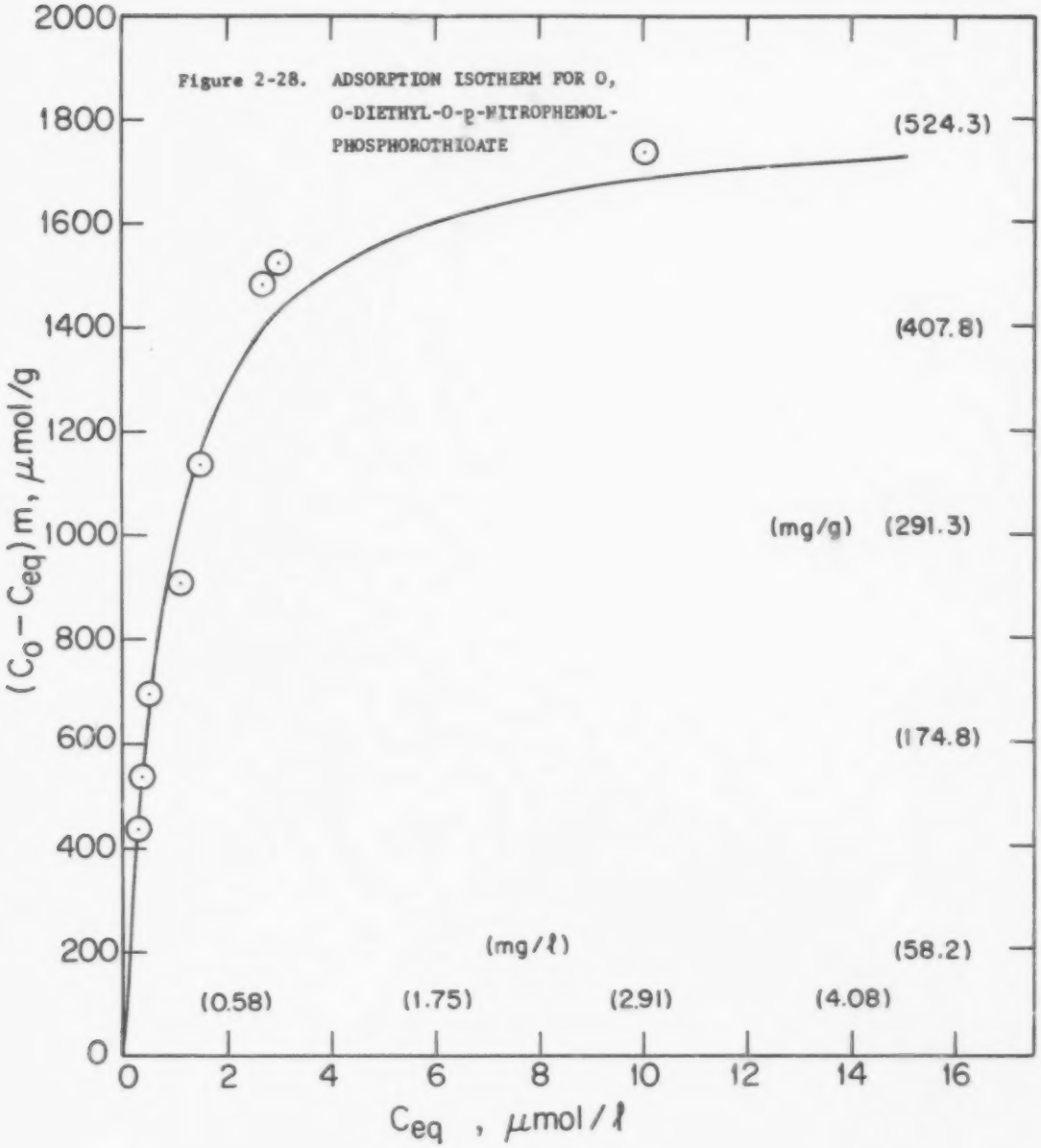

Figure 2-28. ADSORPTION ISOTHERM FOR O, O-DIETHYL-O-p-NITROPHENOL-PHOSPHOROTHIOATE

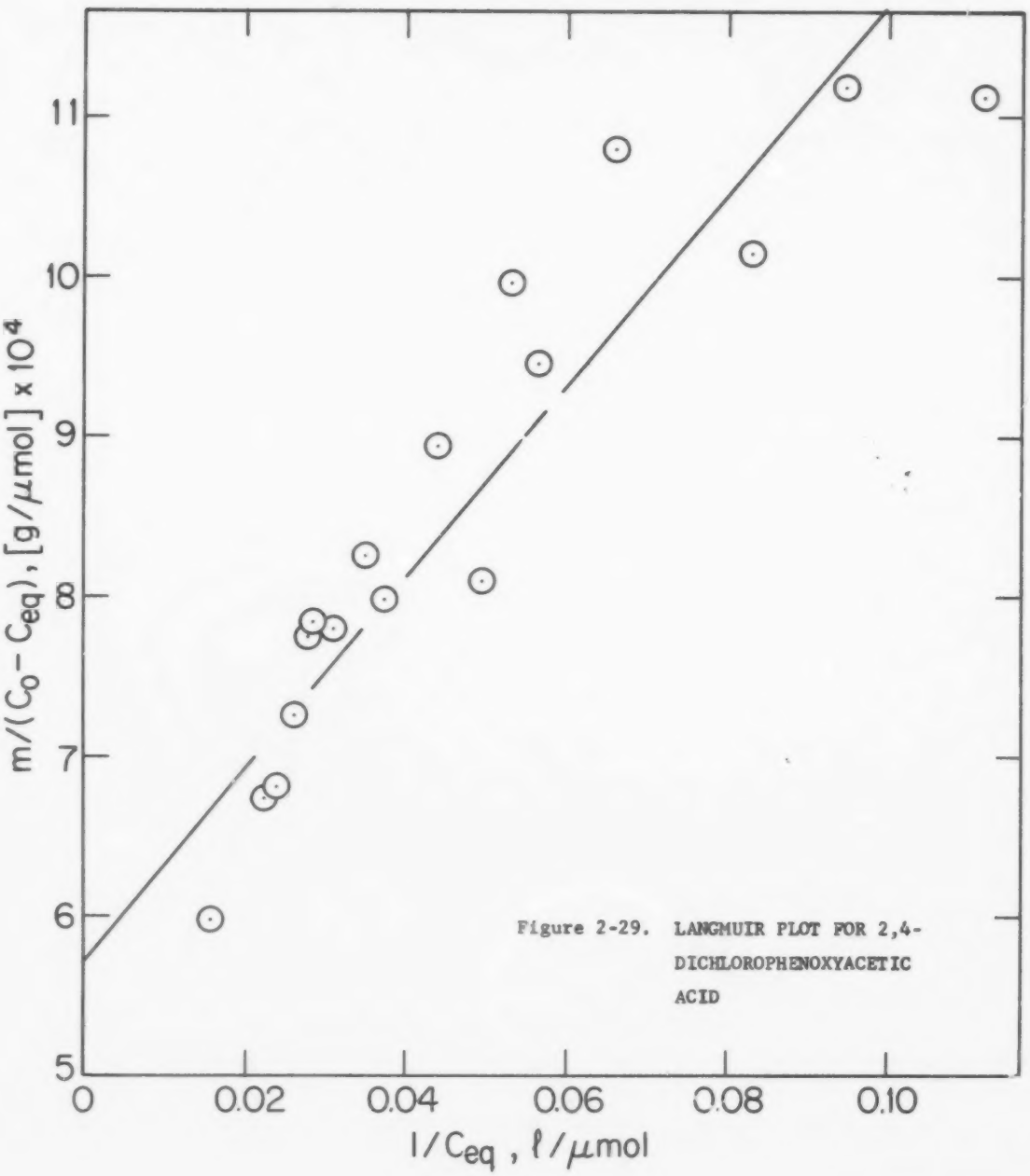

Figure 2-29. LANGMUIR PLOT FOR 2,4-DICHLOROPHENOXYACETIC ACID

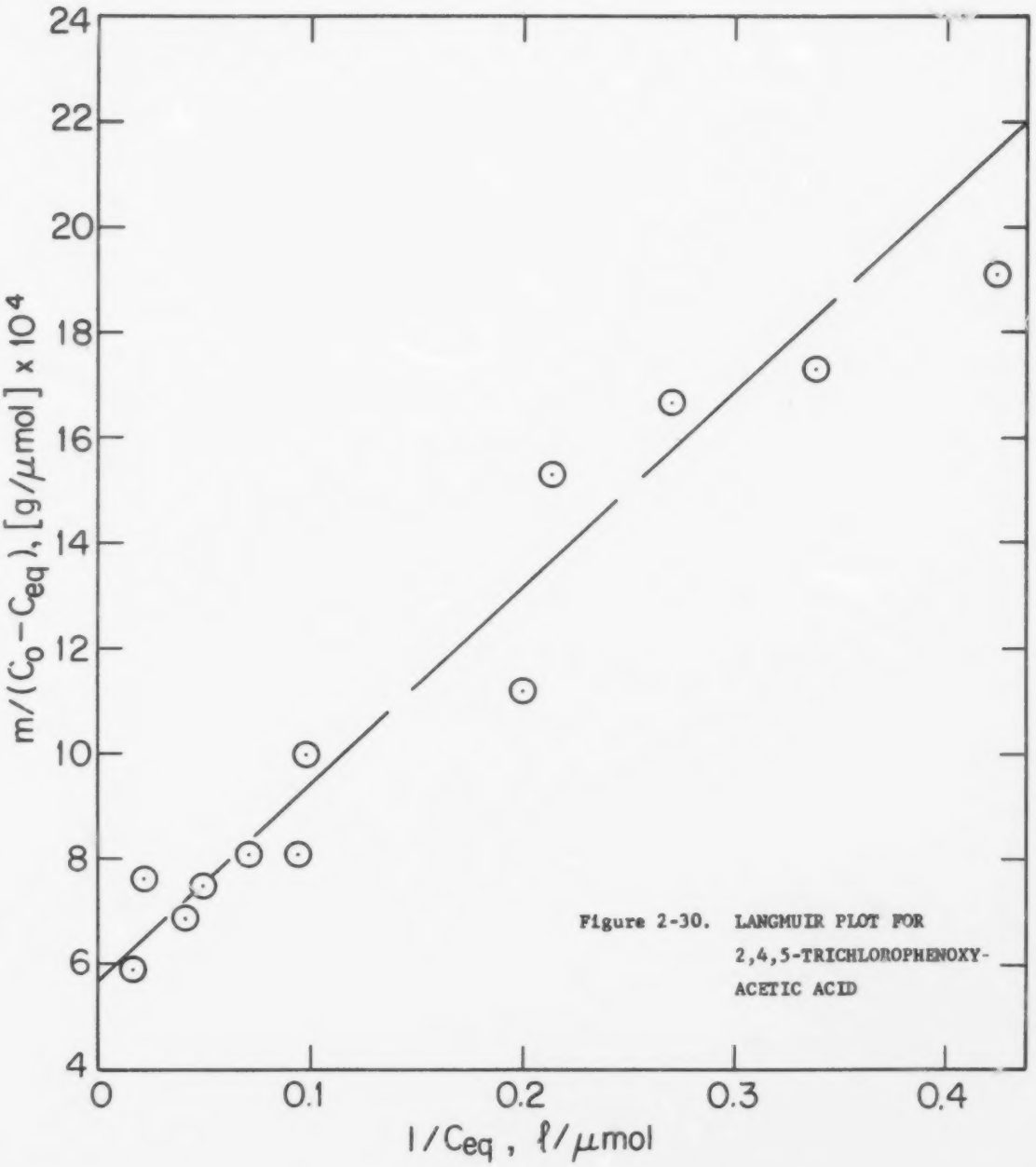

Figure 2-30. LANGMUIR PLOT FOR 2,4,5-TRICHLOROPHENOXY-ACETIC ACID

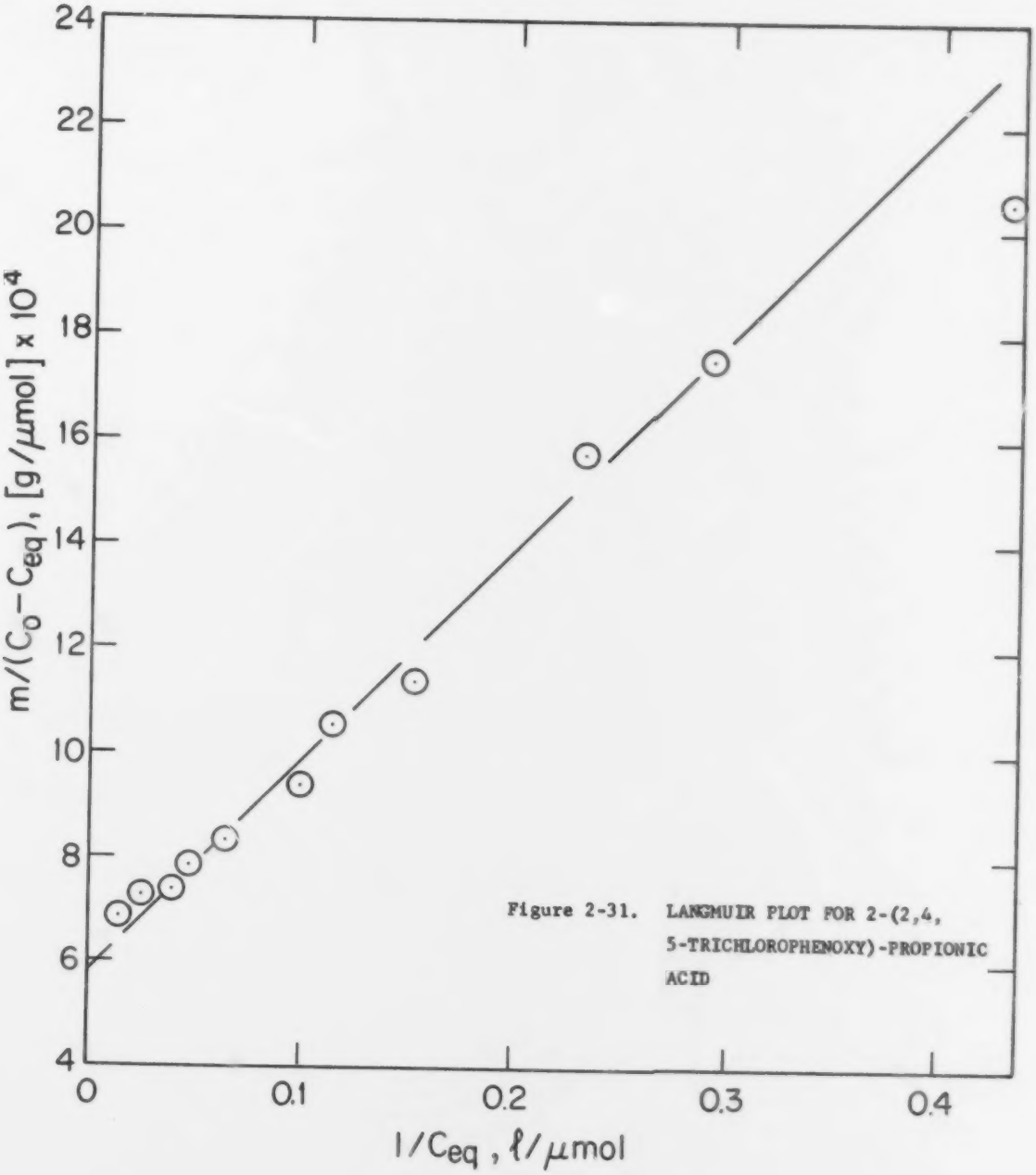

Figure 2-31. LANGMUIR PLOT FOR 2-(2,4, 5-TRICHLOROPHENOXY)-PROPIONIC ACID

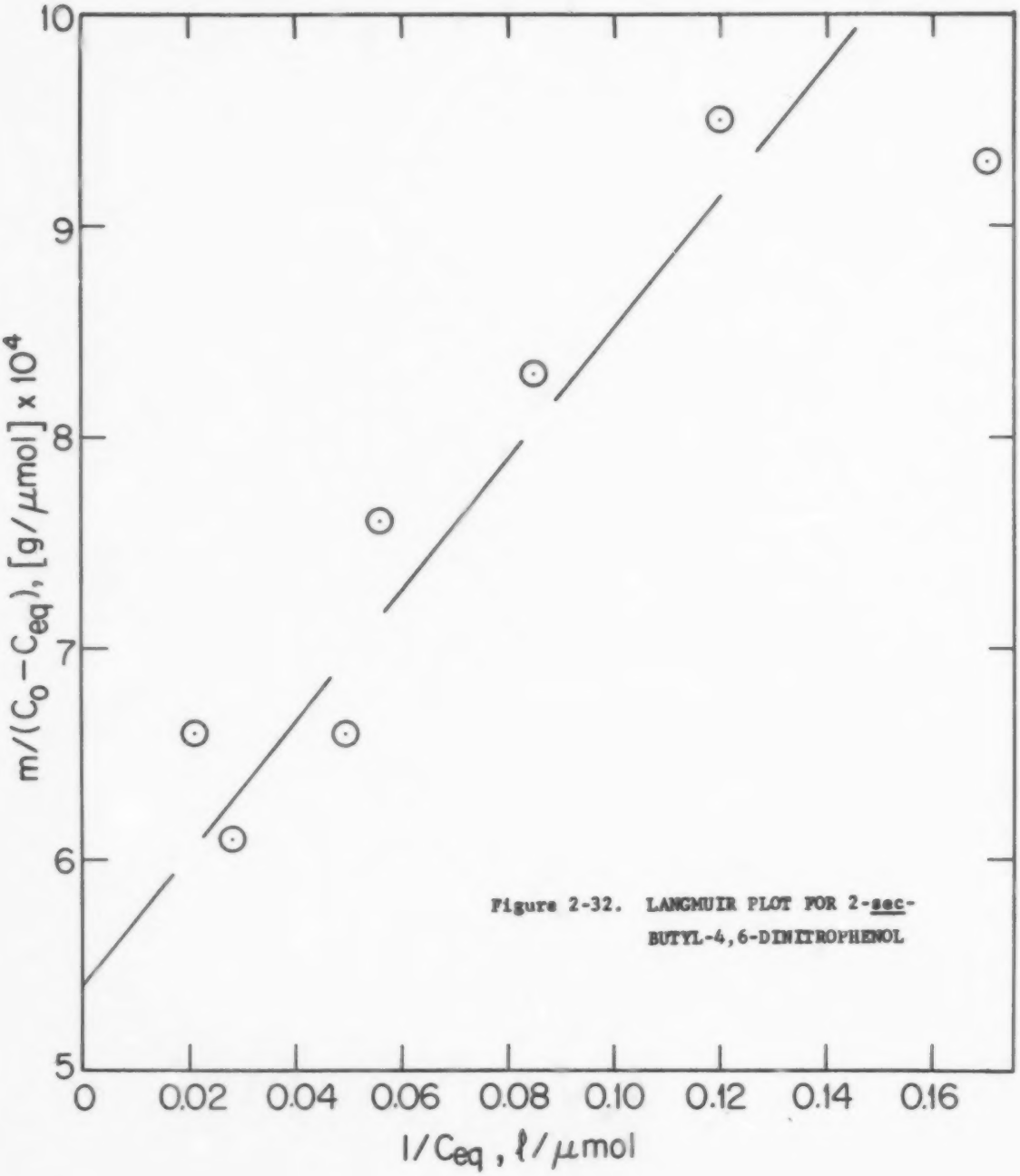

Figure 2-32. LANGMUIR PLOT FOR 2-sec-BUTYL-4,6-DINITROPHENOL

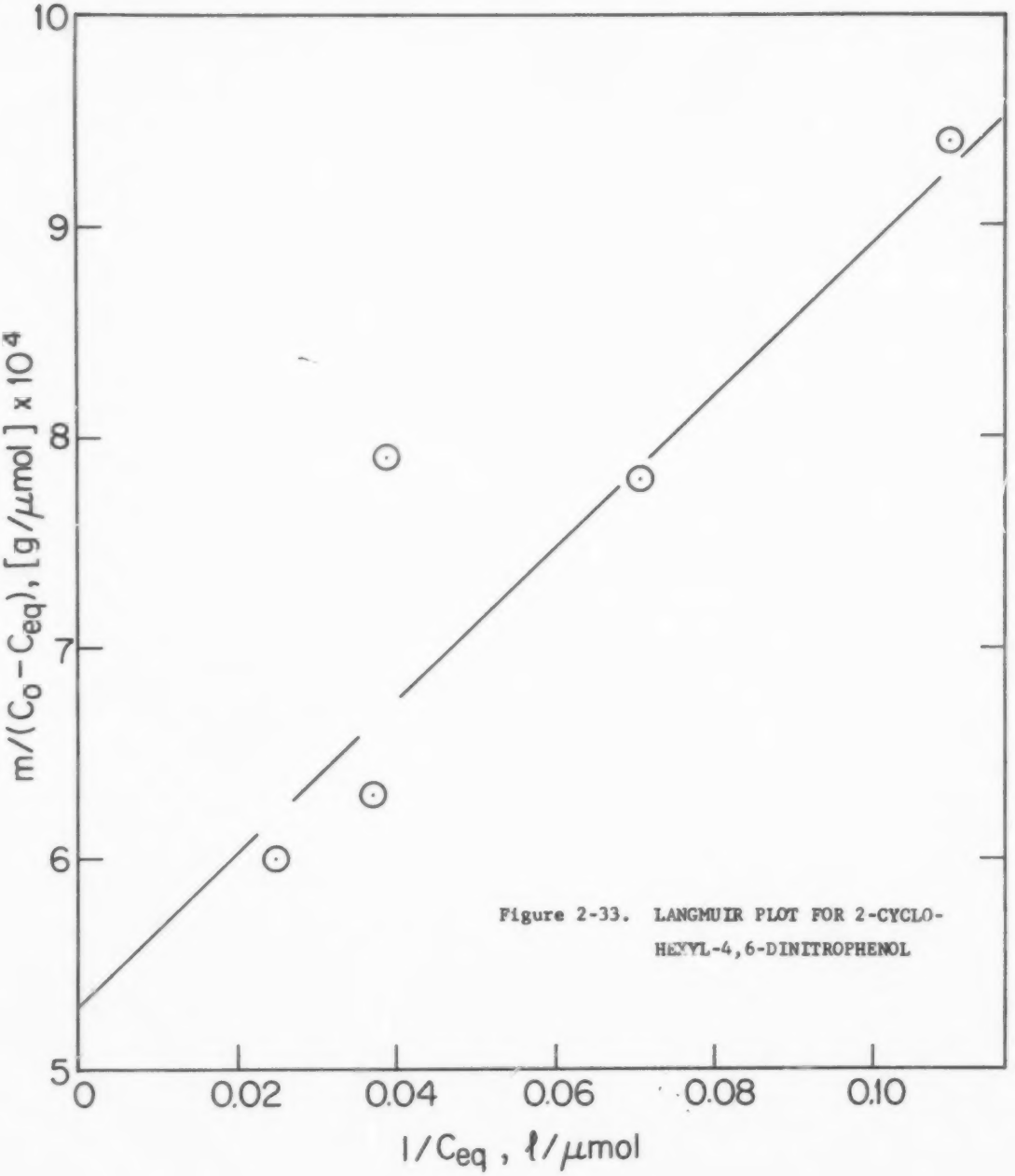

Figure 2-33. LANGMUIR PLOT FOR 2-CYCLOHEXYL-4,6-DINITROPHENOL

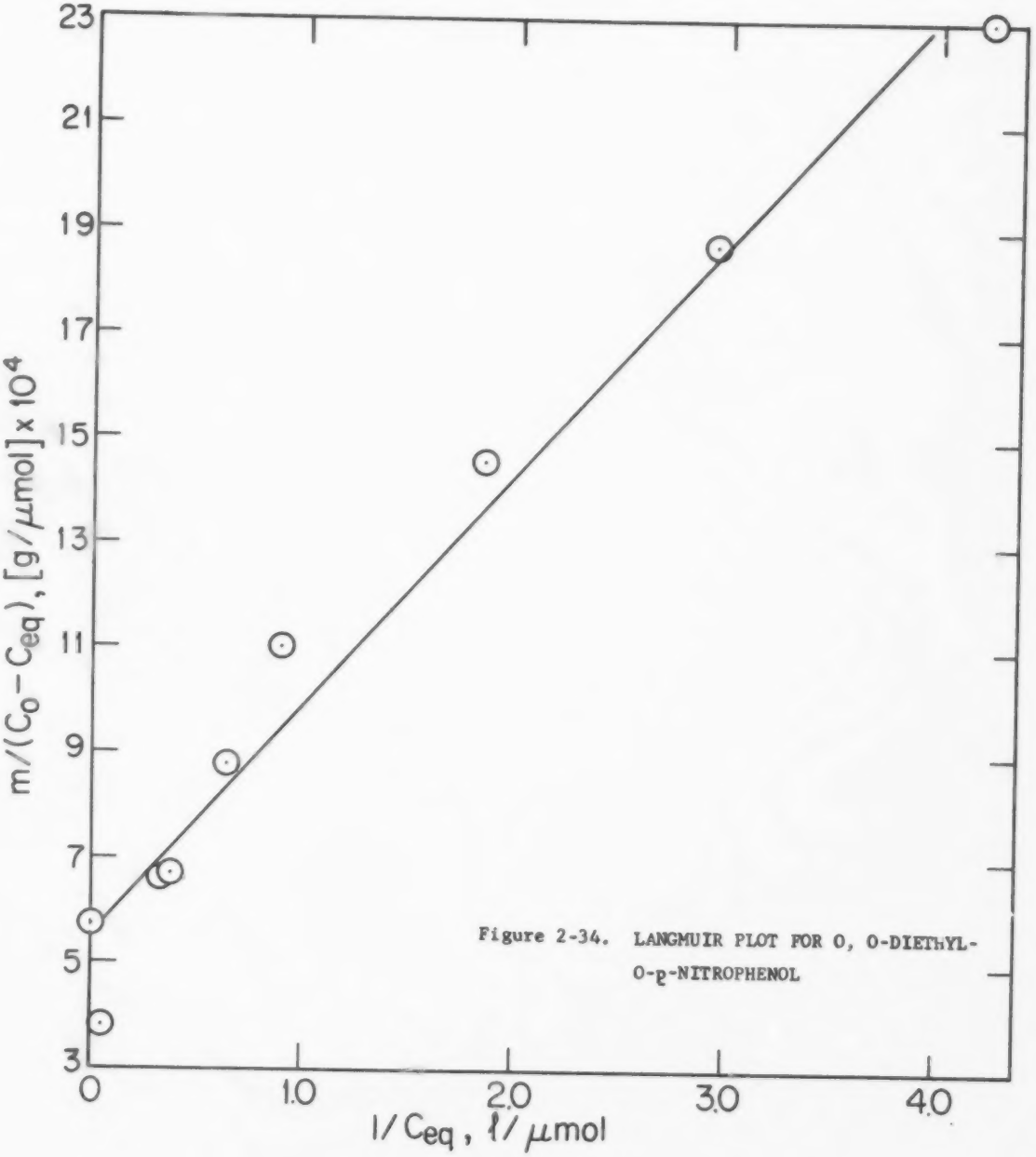

Figure 2-34. LANGMUIR PLOT FOR O, O-DIETHYL-O-p-NITROPHENOL

pesticides indicates that this material has a high energy of adsorption and attains adsorptive capacities near the ultimate capacity at relatively low equilibrium concentrations of solute in solution.

Comparison may also be made between the values of X_m and of b obtained with these pesticides and those obtained earlier for alkylbenzenesulfonates and other compounds. Results of some of these earlier studies along with those for the pesticides are shown in Table 2-5 with somewhat different units than those given in Table 2-4.

Table 2-5

Comparison of Langmuir Constants for Various Adsorbates on Activated Carbon

Compound	X_m, mmol/g	X_m, mg/g	1/b, μmol/l	1/b, mg/l
2,4-D	1.75	387	10.5	2.32
2,4,5-T	1.75	448	6.7	1.71
Silvex	1.72	464	6.9	1.86
DNOSBP	1.85	444	5.8	1.39
DNOCHP	1.88	500	6.8	1.81
Parathion	1.82	530	0.82	0.24
Phenol	1.09	103	9.3	0.87
2-dodecylbenzenesulfonate	0.40	139	0.22	0.078
1-chloro-4-nitrobenzene	2.52	400	1.4	0.22

As can be seen the capacity values for the pesticides are very large, even greater on a weight basis than that previously reported for p-nitrochlorobenzene. On the other hand the 1/b values, except for that of parathion, indicate approach to the saturation adsorption only at relatively high residual concentrations of the adsorbate.

The capacity figures are probably the most significant for column operation, for counter-current operation makes realizable capacities those corresponding to initial concentrations rather than to allowable effluent concentrations. The 1/b values give an indication of the anticipated sharpness of the breakthrough front and to some extent provide guidance for the optimum depth of column for satisfactory removal of the contaminant, although rate of adsorption is an equally important factor in this respect. Larger 1/b values in general would call for greater depths of adsorption column.

Analysis of this type can give only very qualitative conclusions with regard to the pesticides for it is obvious that the basic assumption of the Langmuir treatment, that only a monomolecular layer of adsorbed material is formed, does not hold when one is considering weights of adsorbed material in the neighborhood of 40% of the weight of adsorbent. While the Langmuir formulation does provide an adequate representation of the data for adsorptive equilibrium over a large and relatively high concentration range, it seems likely that more refined experimentation in a lower concentration range (say 1-100 ppb) would show considerably greater adsorption of the pesticides than that predicted by the Langmuir constants presented here. Indeed the experimental results for the lower end of the concentration range shown in Figures 2-26 and 2-27 provide some evidence of this. It seems likely that two different Langmuir formulations may be needed for more exact description, such as those found for phenol in lower and higher ranges of concentration (see pp 61-72, First Annual Report). There the value of X_m at higher concentrations was found to be 3.32 mmol/gram or 310 mg/gram rather than the figures recorded in Table 2-25. It may be noted that the phenol concentrations giving the higher capacity were from 6 to 14% of the saturation values in water. Many of the pesticides were studied in about this range of fractional concentrations of their saturation values.

Consequently, clean-up of small concentrations of pesticides by activated carbon seems likely to be considerably more efficient than indicated by the Langmuir constants obtained in these studies. Problems of initial leakage of these materials are not expected to occur when beds of adequate depth (5-10') of activated carbon are used for advanced waste treatment.

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CHAPTER THREE

EXAMINATION OF EFFLUENTS FROM ACTIVATED CARBON COLUMNS

Studies on the removal of residual organic pollutants from conventionally treated sewage by means of activated carbon have indicated that there is initial leakage of organic material regardless of the extent of carbon treatment.[1] These studies at the Pittsburgh Chemical Company involved conventional filtration of secondary sewage effluents through beds of granular activated carbon five feet in depth, one to three of these units being used in series. Leakage of organic material was measured as chemical oxygen demand in the effluents and was found to be substantially the same after passage through three units as after filtration through a single unit.

The nature of the unadsorbed organic material was not known and is difficult to determine because of the low total concentration and the variety of possible components.

Nonetheless it is of great importance to obtain some idea of the types of substances not effectively removed by carbon adsorption. If these are compounds that have great hygienic significance, then the value of adsorption on carbon as a method for advanced waste treatment is seriously diminished. On the other hand if they are normal bacterial metabolites that have escaped oxidation during conventional sewage treatment or similar compounds, then their presence in small quantity may not represent a significant degradation in effluent quality.

It seemed possible that useful information on the nature of the organic materials might be obtained after concentration of effluent by vacuum distillation. Such treatment would change the effluent by loss of volatile constitutents, but these are not likely to be of importance. Other changes that might occur or their effects are more difficult to assess, but any thermal changes should be minimized by concentrating at as low a temperature as possible.

Accordingly samples of effluent from the carbon columns of the Pittsburgh studies were concentrated by vacuum evaporation at the R. A. Taft Sanitary Engineering Center and two of the concentrates were then shipped to Harvard for examination. Sample number one, which was dated February 7, 1964, had been concentrated by a factor of 36:1, and sample number two, dated May 5, 1964, had been concentrated by a factor of 60:1.

Because of limitations of time not nearly as much was done with these samples as would have been desirable. Besides very general tests only a few determinations of specific types of substances were attempted and the results of these had more significance in a negative sense than in a positive one. Nonetheless, it is believed that the methods of approach have value and that more extensive and detailed examination of similar concentrated effluents from carbon columns should be undertaken by others.

The concentrated effluents as received contained considerable sediment. Much of this was inorganic material such as $CaCO_3$ and $CaSO_4$ that had precipitated during the evaporation. However, some organic matter had also coagulated or precipitated to such an extent that it was removable by filtration through a membrane filter. This may indicate that a part of the organic matter leaking through the columns is colloidal in nature and perhaps therefore either carbohydrate or protein in structure. It would be desirable to pass some unconcentrated effluent through a Seitz or other molecular filter to see how much of the effluent COD would be removed by such treatment. Presumably material of the types indicated would not be particularly deleterious.

It may be noted also that sample number one exhibited rapid growth of microorganisms both during shipment and after receipt. Such growth implies that much of the unadsorbed organic matter in the effluent was readily oxidizable and that failure to be oxidized earlier was the result of one or more of three factors:

(1) The oxidizable materials were originally at too low a concentration for ready biological oxidation and evaporation increased the concentration enough to support good growth of microorganisms.

(2) Organic materials adsorbed by the carbon had been acting as inhibitors for biological oxidation; once they were removed biological metabolism could proceed.

(3) Time of contact in the sewage treatment plant was not great enough for complete oxidation of metabolites.

(4) Short-circuiting in the sewage treatment plant allowed carry-over of some readily oxidized substances.

In any event there is preliminary evidence in this simple observation that a substantial fraction of the organic material leaking through the carbon column is not composed of so-called "persistent" compounds, but may instead be carbohydrates, amino acids or low-molecular weight carboxylic acid salts that would contribute little nuisance to receiving waters ans would tend to be removed by biological oxidation processes in lakes or streams. Also it means that further search for specific unadsorbed materials should not be confined to "exotic" chemicals but should include common metabolites and their intermediates.

Because of this experience a portion of the sample number two was acidified with HCl prior to shipment from Cincinnati to suppress bacterial action.

General measurements that were made on the samples included organic carbon and COD of both total and filtered material, potentiometric acid-base titrations and infra-red examinations of chloroform extractables. Individual measurements of ABS, carbohydrates and dicarboxylic acids were attempted.

Total Organic Carbon

Organic carbon in the effluent samples was determined by the wet oxidation method described by Weber and Morris.[2] For each sample, total organic carbon determinations were performed on the unfiltered material so as to include insoluble organic matter and on samples of the effluent that had been subjected to filtration. The samples were first acidified with sulfuric acid and then oxygen was bubbled through them for ten minutes to remove CO_2.

Results of the determinations, the average of two or three tests in each instance, are shown in Table 3-1 for the samples as received in concentrated form and as computed for the original effluents.

Table 3-1

Determinations of Organic Carbon in Effluents from Pittsburgh Carbon Filters

Sample	Organic Carbon mg/l in concentrate	Organic Carbon mg/l in effluent
No. 1, unfiltered	92	2.6
No. 1, filtered	66	1.8
No. 2, unfiltered	143	2.4
No. 2, filtered	50	0.83

Chemical Oxygen Demand

Determinations of COD were also carried out by the standard technique on unfiltered and filtered samples except that because of the bacterial decomposition in sample No. 1 and other limitations on the sample a measurement on filtered concentrate was not possible for this material. The results of these determinations are shown in Table 3-2.

Table 3-2

Determinations of COD on Effluents from Pittsburgh Carbon Columns

Sample	COD mg/l in concentrate	COD mg/l in effluent
No. 1, unfiltered	398	11.0
No. 2, unfiltered	236	3.9
No. 2, filtered	113	1.9

Ordinarily one may expect the COD value for a waste to be about 2.5 to 3 times the organic carbon, the theoretical ratio for carbon in the zero oxidation state as in carbohydrate being 32/12 or 2.67. Also, the total weight of organic matter will range around 2.5 times the organic carbon - 30/12 or 2.5 being the value for a simple carbohydrate. Thus for organic material with average oxidation number near zero COD and total weight of organic matter will be approximately the same numerically.

However, the two factors tend to change in opposite directions as the average oxidation number departs from zero. With butyric acid $C_4H_{10}O_2$ with a mean oxidation number of -1.5 for the carbon the weight is 1.875 times the organic carbon while the COD should be 3.67 times the organic carbon. Similarly, for glyoxylic acid, $C_2H_4O_3$, with net carbon oxidation number of + 1, the weight is 3.17 times the organic carbon while the COD is only 2.0 times it.

Filtered sample No. 2 shows an expected ratio between COD and organic carbon, 113/50 or 2.26. If this ratio is accurate, the mean oxidation state of the carbon in the effluent is relatively high, about + .6. Such a result seems in accord with the fact that this effluent had already been subjected to considerable oxidative treatment and is also in accord with the intuitive

feeling that oxygenated organic compounds such as dicarboxylic acids which will exist in wastes as ionized materials will be less readily adsorbed by carbon than other types of organic substances.

The ratios of COD to organic carbon for the unfiltered effluents, 4.33 for sample No. 1 and 1.65 for sample No. 2, are completely outside the range of legitimate values for the type of material being studied. Variations in sampling of the suspended matter or failure to achieve complete COD for suspended organic matter may have caused these anomalies.

Acid-Base Titrations

Because it seemed likely that carboxylic acid salts might be largely responsible for the observed leakage of organic material through carbon beds, it was felt that potentiometric acid-base titration curves on the effluent concentrates would be useful in characterizing the organic materials.

Accordingly such titrations were performed on portions of the concentrates that had been filtered through membrane filters. Titrations were carried out on 25-ml portions of sample No. 1 and 50-ml portions of sample No. 2, pH readings with a glass electrode being taken frequently throughout the titrations with tenth-normal HCl or KOH. The results of these titrations, shown in Figures 3-1 and 3-2, were unsatisfactory largely because the dominating effect of the high concentrations of carbon dioxide and bicarbonate alkalinity had been overlooked.

Additional titrations were therefore performed on portions of filtered sample No. 2 which had been acidified and aerated to remove CO_2 before titration with tenth-normal hydroxide. Results of this work are shown in Figure 3-3.

Again the results were unsatisfactory, because the excess of acid used had been too great so that neutralization of this strong acid tended to obscure the finer points of the titration curve. There was some indication

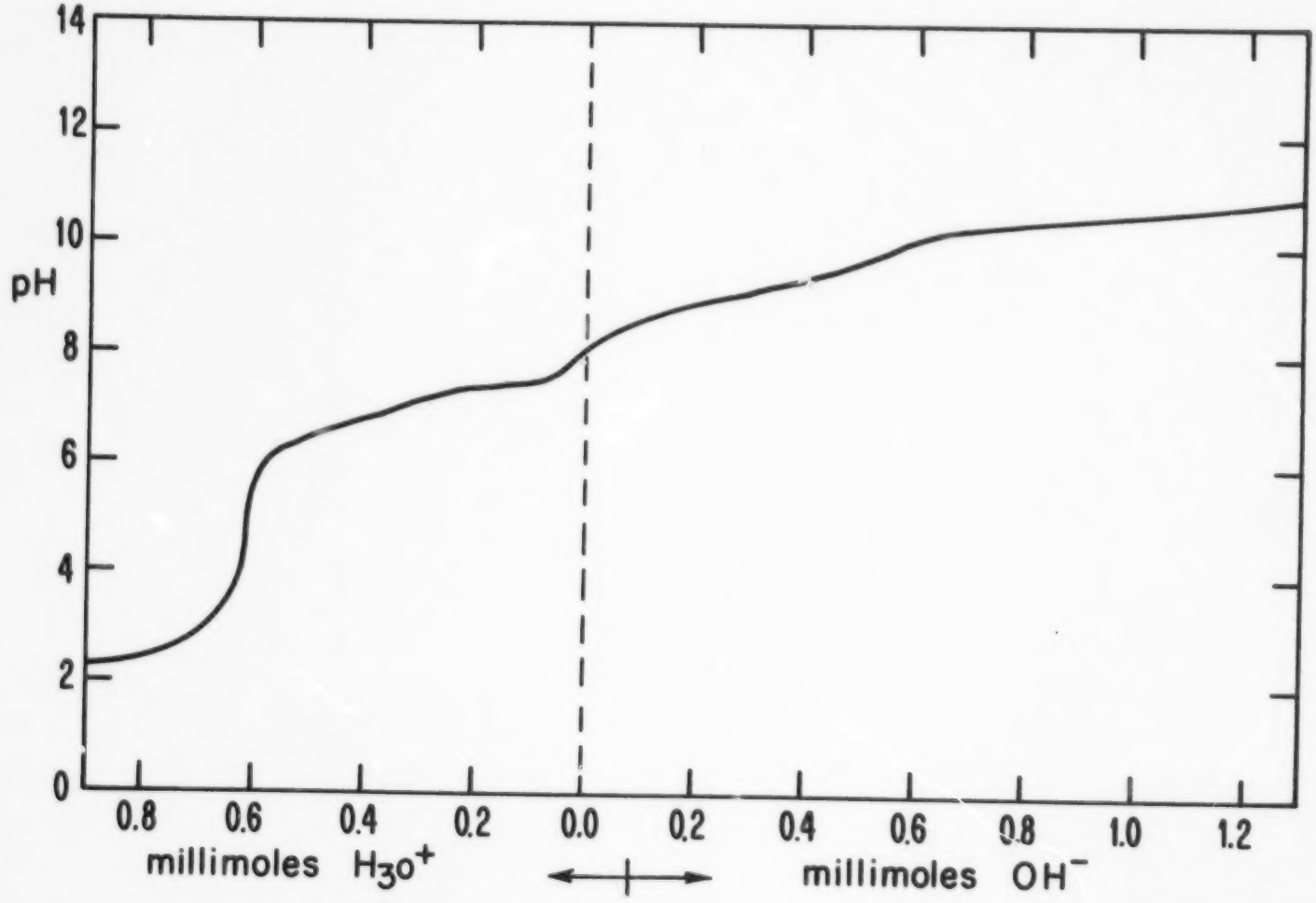

Fig. 3-1 Titration of EFFLUENT No. 1 25-ml sample

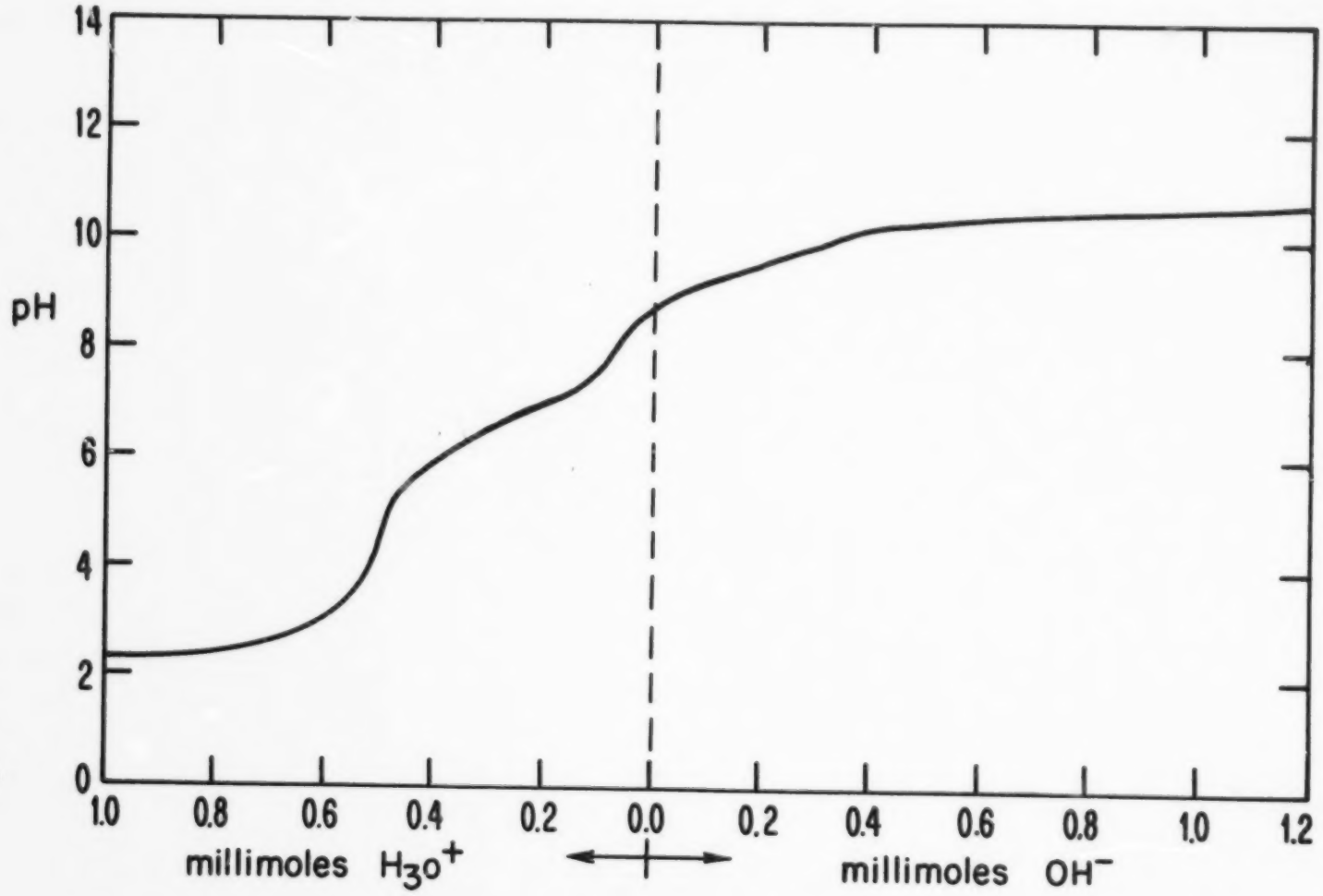

Fig. 3-2 Titration of EFFLUENT No. 2 50-ml sample

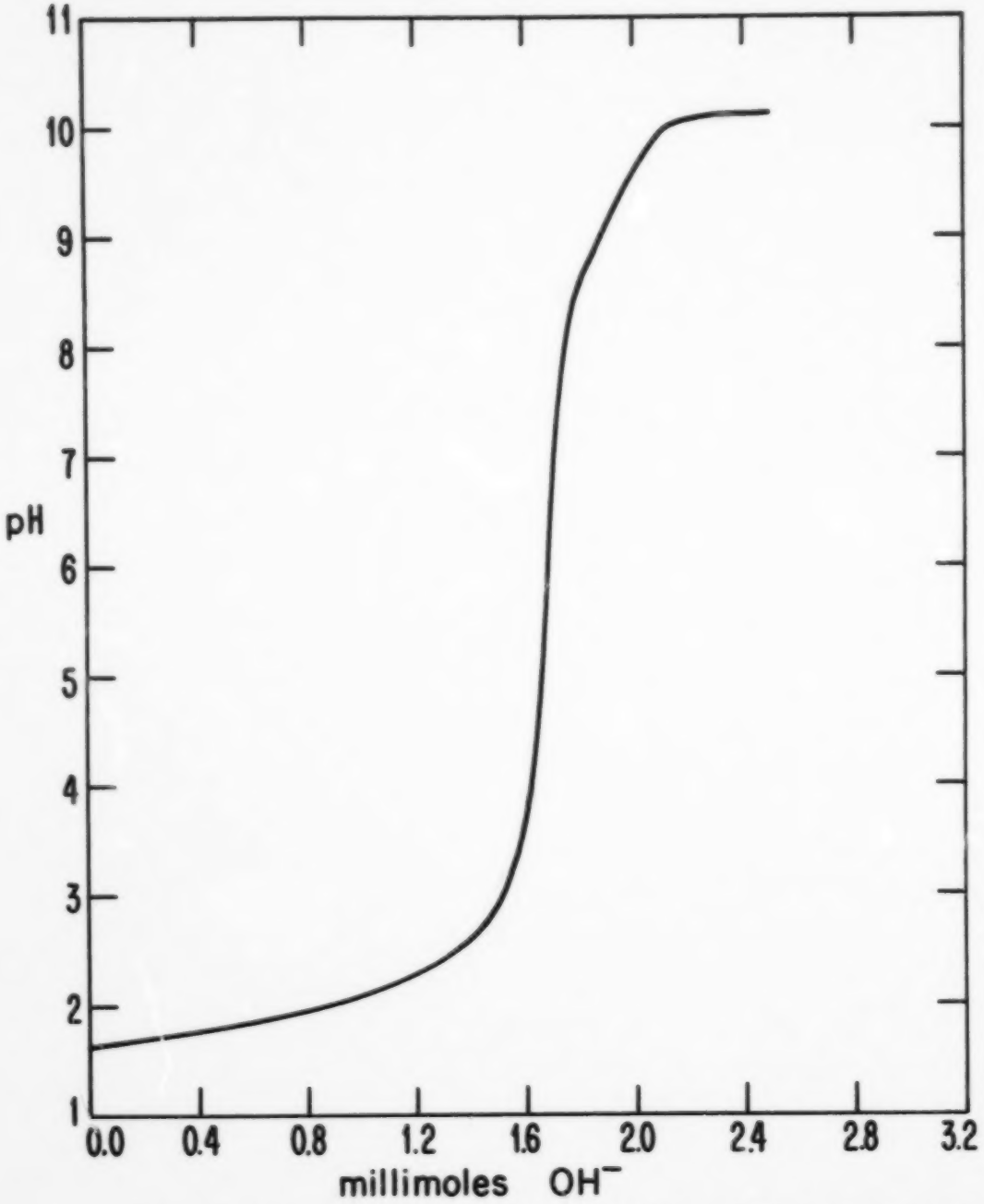

Fig. 3-3 Titration of acidified EFFLUENT No. 1
50 ml-sample

of weakly basic sonstituents in the form of the titration curve near pH-10, possibly an indication of amino acids, but because precautions to remove ammonia and phosphate had not been taken the data must be considered inconclusive.

In spite of the failure of these titrations it is still believed that valuable information can be obtained from similar titrations carried out after more careful preparation of the initial solutions. Based on the experience obtained preliminary treatment should include the following steps: (1) Acidification of total unfiltered sample to pH 4 ± 0.5 followed by bubbling of nitrogen through the sample to remove CO_2 fully; neutralization with CO_2-free KOH, possibly accompanied by addition of Ca^{++} or some other precipitating ion, (La^{+++})?, to remove $PO_4^{\equiv}$ completely, followed by filtration (not necessarily through a membrane filter; it may be desirable to include colloidal material in the titration); (2) Addition of CO_2-free KOH to pH 9.5 followed by bubbling of nitrogen to remove NH_3 fully. At this point the sample should be separated into two portions, one to be titrated carefully with dilute acid, the other with dilute base. As nearly continuous records of pH as a function of acid or base added should be obtained and compared with similar curves for the titration of CO_2-free distilled water.

ABS Determinations

Each of the concentrates was analysed for ABS concentration by the methylene blue method as given in Standard Methods.[3]

Concentrations were determined from a calibration curve obtained for a technical ABS, Ultrawet DS, obtained from the Atlantic Refining Company, having a molecular weight of 372.[4] The Ultrawet DS solutions used for the calibration of the methylene-blue method were standardized by ultraviolet spectrophotometry.[4]

Sample No. 1 was determined to have an ABS concentration of 6.0 mg/l, and sample No. 2 an ABS concentration of 7.0 mg/l. Considerable difficulty was experienced with both effluents during the ABS tests due to emulsion formation.

These values for ABS concentration in the concentrates correspond to 0.17 mg/l in the original effluent No. 1 and to 0.12 mg/l in effluent No. 2, values that accord well with expectations for effluents from carbon columns and with similar analyses performed at Cincinnati.

Miscellaneous Specific Tests

All of the additional work carried out was on sample No. 2 because of the bacterial degradation that occurred rapidly in sample No. 1.

Attempts were made to find chloroform-extractable materials in the concentrate by treatment with this reagent followed by infra-red examination of the dried chloroform extracts. Only negative results were obtained with the concentrates as received and attempts to work with more highly evaporated solutions were frustrated by the formation of highly stable emulsions. Time did not permit further explorations along this line.

Glucose and total carbohydrate determinations were carried out, the former by the glucostat enzymatic method, the latter by the anthrone method as described by Gaudy.[5] Results for glucose were negative as might well have been expected, but carbohydrate was found at a concentration of 7 mg/l in the concentrate, corresponding to 0.12 mg/l in the initial effluent. One might guess that this material would be dextrin-like in nature, degraded glycogen or cellulose perhaps.

Some experimentation was done with thin-layer chromatography on the effluent samples. Qualitative indication of the presence of small quantities of dicarboxylic acids was obtained, but methods for quantitative estimation of the amount were not at hand. The technique does show promise for examination

of these effluents and probably should be pursued more intensively in the future.

It is unfortunate that circumstances prevented extension of these investigations, for additional general information could have been obtained readily. For example, determinations of Kjeldahl nitrogen and organic phosphorus would have helped greatly in characterizing the residues and these can be performed easily. More sophisticated techniques such as gas chromatography were proposed, but could not be used because of delays in obtaining appropriate equipment.

Summary and Conclusions

Perhaps the most significant result of this preliminary and partial investigation into the nature of the organic material unadsorbed by activated carbon columns is a negative one. No indications were found of important amounts of the persistent, noxious organic chemicals for which methods of removal are most important. What positive data could be obtained makes it seem likely that partially oxidized substrates and metabolites of microorganisms make up a major portion of the effluent organic matter. Although this conclusion is not a firm one, nothing that has been found gives any reason to suppose that further development of full-scale equipment for advanced waste treatment by activated carbon should be drastically modified or abandoned.

Besides the obvious step of continued experimentation along the lines followed in these tests to find individual compounds or classes of compounds contributing to the organic leakage, another method of approach is to test likely individual substances or classes of materials to see how they behave on carbon columns. Dilute solutions of individual carbohydrates, carboxylic acids, amino acids and so forth might be passed through laboratory-scale columns to see how effectively they are removed.

It may be noted that in the small column studies described in Chapter 1 of this report the material that gave greatest difficulty with leakage was triethanolamine, a small, hydroxlated molecule existing largely in salt-like cationic form in neutral aqueous solutions. In contrast all materials containing phenolic groups seem to be quite effectively adsorbed.

It appears that, if additional removal of organic matter beyond that now obtainable with reasonable depth of activated carbon is desired, one should follow the activated carbon with a contrasting type of adsorbent. One possibility seems to be to make use of porous or so-called "macro-reticular" ion-exchange resins in this way, taking advantage of their adsorptive abilities rather than specifically of their ion exchange properties. Organic "fouling" of ion-exchange resins is well-known and there is reason to suppose that the types of materials causing fouling may be like those leaking through carbon columns.

It is recommended that experimentation be initiated to investigate possibilities along these lines.

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